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FURTHER STUDIES ON THE DEVELOPMENT OF A VACUUM PYROLYSIS PROCESS FOR LIGNOCELLULOSICS

RENEWABLE ENERGY BRANCH

PREPARED FOR:

Renewable Energy Branch
Energy, Mines and Resources Canada
Ottawa, Canada
DSS Contract File No: 05SV.23216-4-6190
Report Submitted June 30, 1986

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CONTRACT CITATION

Roy, C., R. Lemieux, B. de Caumia, D. Blanchette and H. Pakdel, Université de Sherbrooke. Further studies on the Development of a Vacuum Pyrolysis Process for Lignocellulosics, Report of Contract File #05SV.23216-4-6190. Renewable Energy Branch; Energy, Mines and Resources Canada, Ottawa, Ontario. 1986. (68 pp.).

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ACKNOWLEDGEMENTS

The following individuals are gratefully acknowledged for their participation in this study: Mr. Jean Fréchette, Mr. Blaise Labrecque and Miss Sylvie Béland.

PREFACE

The work performed under this contract was a 15 month extension of that done under three previous contracts (ENFOR C-33, C-256 and C-326 projects). The first of these was awarded in 1979, ended in 1982, and dealt with some fundamental aspects of vacuum pyrolysis of wood. Project C-326 started in 1982 and was completed in 1984. It involved the design, construction and preliminary operation of a Process Development Unit (P.D.U.) for the vacuum pyrolysis of lignocellulosics. Project C-256 was conducted from 1981 to 1982 and was related to the chemical characterization of wood-derived oils.

The intended purpose of this study was to obtain new data leading to engineering calculations for the development of the vacuum pyrolysis process. Scope of the work included mass and energy balances around the reactor and a study of the heat transfer phenomena in the pyrolysis reactor. The capability of the Process Development Unit to produce and separate various types of oils was also investigated.

This work fits within the general objectives of the Renewable Energy Branch where a better use of biomass as a source of fuels and chemicals is one of the goals of the program. The vacuum pyrolysis approach is one of the thermoconversion routes which are currently being supported in Canada by the Renewable Energy Branch. The intended audience for this report is, apart from the Renewable Energy Branch officials, the other contractors in the field, representatives of the biomass industry in Canada and elsewhere, equipment manufacturers and the scientific community in general.

ABSTRACT

The objectives of this study were 1) to confirm the influence of temperature and pressure on oil yields during vacuum pyrolysis of biomass using a Process Development Unit, 2) to improve the energy data base for the vacuum pyrolysis process, 3) to improve our knowledge of heat transfer phenomena during pyrolysis reactions and 4), to ascertain the capability of the Process Development Unit to simultaneously produce and separate various types of oils at the reactor outlets. This was done using a multiple hearth furnace, 2 m in height and 0.7 m in diameter. The reactor which comprised six hearths, was electrically heated. The throughput capacity of the Process Development Unit was about 2 kg h^{-1} for this work.

Oil yields in the range of 50 kg/100 kg of wood feedstock (organic basis) have been confirmed based on mass balances better than 96%. Both temperature and pressure have a strong influence on the oil yields. The required energy for conducting the pyrolytic reactions has been determined to be 615 kJ kg^{-1} (147 kcal kg^{-1}) of anhydrous wood under a vacuum. The overall heat transfer coefficient for the reactor has been estimated at 92 kJ h^{-1} m^{-2} $°C^{-1}$ (22 kcal h^{-1} m^{-2} $°C^{-1}$). It is also possible to separate the aqueous phase product from the bulk of the organic liquid phase with this Unit. These results make the vacuum pyrolysis approach attractive and promising. The methodology used during this work to determine the pyrolysis energy requirement and to study the heat transfer phenomena can also benefit other researchers.

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EXECUTIVE SUMMARY

The work performed under this contract was a 15 month extension of that done under three previous contracts (ENFOR C-33, C-256 and C-326 projects). The study was conducted between October 10, 1984 and December 31, 1985. The first contract was signed in 1979, ended in 1982, and dealt with some fundamental aspects of vacuum pyrolysis of wood. Project C-326 started in 1982 and was completed in 1984. It involved the design, construction and preliminary operation of a Process Development Unit (P.D.U.) for the vacuum pyrolysis of lignocellulosics. Project C-256 was conducted during 1981 and 1982 and was related to the chemical characterization of wood-derived oils.

The objectives of this study were 1) to confirm the influence of temperature and pressure on oil yields during vacuum pyrolysis of biomass using a Process Development Unit, 2) to improve the energy data base for the vacuum pyrolysis process, 3) to improve our knowledge of heat transfer phenomena during pyrolysis reactions and 4), to ascertain the capability of the Process Development Unit to simultaneously produce and separate various types of oils at the reactor outlets.

The study was conducted using a vacuum pyrolysis Process Development Unit. The reactor was a multiple hearth furnace, 2 m high and 0.7 m in diameter, with six hearths. Heat transfer was provided through heating elements. The reactor, which was fed in a semi-continuous mode with wood chips, had a throughput capacity of about 2 kg h^{-1}. The heating plate temperatures increased from top to bottom of the reactor. A typical temperature profile was 200°C to 450°C. The total pressure in the system was lower than 10.7

kPa (80 mm Hg) under steady state conditions. The experiments were performed using Populus deltoides as wood feedstock. Approximately 75 parameters were routinely recorded as a function of time, and real time energy balance was routinely performed with this Unit.

Maximum oil yields in the range of 50% by weight (wood organic basis) have been confirmed based on mass balances better than 96%. The calorific value of this oil is about 15 635 kJ kg^{-1}. Other products include charcoal (21-25%), gas (11-140%) and pyrolytic water (17-20%). The optimum reactor temperature for high yields of oils is between 425°C and 450°C at low vacuum pressure conditions. Pressure, however, has a very significant effect on oil yields, more important than originally observed under laboratory conditions. For instance, increasing the reactor pressure from 1.6 to 10.7 kPa (absolute), at similar temperature conditions, resulted in a drop in oil yield from 50.5% down to 40.8%.

The required energy for conducting the pyrolytic reactions has been determined to be 615 kJ kg^{-1} (147 kcal kg^{-1}) of anhydrous wood under a vacuum. Heat removed at the primary cooling stage to recover organic liquids has been found to be 452 kJ kg^{-1} (108 kcal kg^{-1}) of anhydrous wood. Heat removed at the secondary cooling stage is negligible in front of the first stage. The energy balance around the reactor is about 96.5%. The heating value of raw wood is almost equally distributed between oil and charcoal products. At this stage of the work it has not been possible to determine the energy efficiency of the process.

Heat transfer phenomena within the reactor have been given some consideration. Heat transfer was assumed to be mainly via conduction at reactor temperatures below 450°C. A simple model has been conceived with the furnace operating like a heat exchanger. The model led to an overall heat transfer coefficient (U) with a value of 92 kJ h^{-1} m^{-2} $°C^{-1}$ (22 kcal h^{-1} m^{-2} $°C^{-1}$). The U value can be used for comparison purposes. The model can still be improved. It has not been possible to determine the Uc value for the shell and tube heat exchangers during this study.

Analyses of the wood oil product showed that a separation of the aqueous phase from the organic liquid phase can be achieved by controlling both the cooling temperature and the pressure within the system. Whether a selective separation of the different kinds of organic liquids at the six outlets of the reactor can be achieved is still unclear at this stage of the study.

It is the view of the authors of this report that the data brought by this work are of great importance for the further development of the vacuum pyrolysis process. More work is needed however in order to complete the design of the final Unit.

RESUME

Ce travail a été exécuté sous contrat durant une période de quinze mois ayant débuté le 10 octobre 1984 et s'étant achevée le 31 décembre 1985. Il fait suite à trois autres contrats précédents sur le même sujet, portant les numéros ENFOR C-33, ENFOR C-256 et ENFOR C-326. Le premier de ces contrats avait été accordé en 1979 et s'était terminé en 1982; celui-ci portait sur des aspects fondamentaux de la pyrolyse sous vide du bois. Le projet C-326 a débuté en 1982 pour se terminer en 1984. Celui-ci portait sur le design, la construction et l'opération préliminaire d'une Unité de Développement de Procédé (U.D.P.) pour la pyrolyse sous vide de matières lignocellulosiques. Enfin le projet C-256 a été mené entre 1981 et 1982 et était relié aux aspects de caractérisation chimique des huiles dérivées du bois.

Cette étude avait pour objectifs 1) de vérifier et de confirmer l'importance du rôle de la température et de la pression sur les rendements en huiles durant la pyrolyse sous vide de la biomasse dans une U.D.P., 2) d'améliorer notre connaissance du bilan d'énergie pour le procédé, 3) d'améliorer également notre connaissance générale des phénomènes de transfert de chaleur dans le réacteur et 4) d'établir la capacité de l'U.D.P. en question de produire et de séparer simultanément différents grades d'huiles pyrolytiques à la sortie du réacteur.

L'étude a été effectuée à l'aide d'une Unité de Développement de Procédé (U.D.P.) pour la pyrolyse sous vide. Le réacteur consiste d'un four à six soles multiples, de dimension de 2 m par 0.7 m de diamètre. Le transfert

de chaleur dans le réacteur se fait au moyen d'éléments chauffants électriques. Le four était alimenté de façon semi-continue au moyen de copeaux de bois de Populus deltoides à un débit maximum de 2 kg h^{-1}. La température des plateaux du réacteur allait croissante depuis le haut jusque vers le bas du réacteur. Typiquement, un profil de température utilisé avec ce réacteur était 200°C dans le haut, et 450°C dans le bas. La pression totale du système était inférieure à 10.7 kPa (80 mm Hg) aux conditions de régime. On pouvait enregistrer 75 paramètres différents avec cette U.D.P. qui permettait également d'effectuer un bilan d'énergie en temps réel.

On a confirmé que les rendements massiques maximums en huiles pyrolytiques étaient de l'ordre de 50% sur la base du bois sec alimenté, et sans cendres. La valeur calorifique de ces huiles est de l'ordre de 15 635 kJ kg^{-1}. Les autres produits pyrolytiques sont le charbon (21-25%), le gaz (11-14%) et l'eau pyrolytique (17-20%). Les bilans de masse sont meilleurs que 96%. La température de pyrogénation optimale pour atteindre ces rendements élevés en huiles se situe entre 425 et 450°C (température des plaques chauffantes). La pression a également une grande influence sur les rendements obtenus en huiles, influence plus forte que ne l'avaient laissé supposer les études initiales à l'échelle du laboratoire. Ainsi, une augmentation de la pression totale de 1.6 à 10.7 kPa, pour des conditions de température de pyrolyse identiques, entraîne une chute dans les rendements en huiles de 50.5% à 40.8%.

L'énergie requise pour effectuer les réactions de pyrolyse sous vide a été déterminée empiriquement, et équivaut à 615 kJ kg^{-1} (147 kcal kg^{-1}) de bois

anhydre. La quantité de chaleur échangée au niveau du système de refroidissement primaire pour la récupération de la phase liquide organique a été établie à 452 kJ kg^{-1} (108 kcal kg^{-1}) de bois anhydre. La quantité de chaleur échangée au niveau du système de refroidissement secondaire est négligeable dans ce système. Le bilan d'énergie autour du réacteur se situe à 97.5%. Le pouvoir calorifique de la biomasse de départ est à peu près également distribué entre les produits principaux: huiles pyrolytiques et charbon de bois. Il n'a pas été possible cependant à cette étape-ci de nos travaux d'évaluer précisément l'efficacité thermique globale du procédé.

On a aussi étudié les phénomènes de transfert de chaleur dans le réacteur de pyrolyse. On a assumé que le transfert de chaleur s'effectue principalement par conduction à des températures inférieures à 450°C. Dans ces conditions, on a conçu un modèle simple de transfert de chaleur où le four de pyrolyse opère comme un échangeur de chaleur. Ceci nous a conduit à déterminer un coefficient global de transfert de chaleur (U) dont la valeur est 92 kJ h^{-1} m^{-2} $°C^{-1}$ (22 kcal h^{-1} m^{-2} $°C^{-1}$). Même si le modèle utilisé est imparfait et peut être amélioré, la valeur trouvée pour U est utile pour fin de comparaison. Par contre, il n'a pas été possible de déterminer au cours de cette étude la valeur Uc pour les échangeurs de chaleur de l'unité de refroidissement primaire.

L'analyse des condensats liquides produits a démontré qu'il était possible de séparer la phase aqueuse de la phase organique, au moyen d'un ajustement de la température de refroidissement des condenseurs et de la pression du système. Toutefois à cette étape-ci de nos travaux, il ne nous est pas

possible de dire si une récupération sélective des huiles pyrolytiques aux six sorties du réacteur est réalisable.

Les auteurs de ce rapport sont d'avis que les nouvelles données forunies par la présente étude sont très utiles en vue du futur développement du procédé de pyrolyse sous vide. Des études ultérieures sont toutefois encore requises afin de compléter le design final du procédé.

1. INTRODUCTION

The work performed under this contract was a 15 month extension of that done under three previous contracts (ENFOR C-33, C-256 and C-326 projects). The first of these was awarded in 1979, ended in 1982, and dealt with some fundamental aspects of vacuum pyrolysis of wood. Project C-326 started in 1982 and was completed in 1984. It involved the design, construction and premilimary operation of a Process Development Unit (P.D.U.) for the vacuum pyrolysis of lignocellulosics. Project C-256 was conducted from 1981 to 1982 and was related to the chemical characterization of wood-derived oils.

These studies led to the conclusion that vacuum pyrolysis is a valuable concept for the upgrading of lignocellulosics into liquid fuels and chemicals. The optimum operating conditions (e.g., temperature, pressure, particle size...) were studied at the laboratory scale and some of these conditions were subsequently tested at the P.D.U. level. The oil yields have been confirmed in the semi-continuous system, and the preliminary results were confirmed with good mass balances. However, some important engineering information like the energy data base were totally absent from the first studies. The current work was then undertaken, with the main goal to answer questions regarding the energy balance and energy requirements of the reaction.

2. OBJECTIVES

The objectives of the study were as follows:

- Improve the construction and configuration of the Process Development Unit for smoother operation and greater reliability.

- At least double the throughput capacity of the main reactor.

- Confirm the influence of temperature and pressure on oil yields with the P.D.U., by comparing them with the results obtained at the batch laboratory scale.

- Improve the energy data base for the vacuum pyrolysis process. More specifically, the reaction energy requirements should be calculated, and the energy balance around the reactor should be estimated.

- Improve our knowledge of heat transfer phenomena within the pyrolysis reactor.

- Ascertain the capability of the P.D.U. to simultaneously produce and separate various types of oils at the six reactor outlets.

3- METHOD

3.1 Vacuum Pyrolysis Process Development Unit

A shematic of the Process Development Unit (P.D.U.) used in this study is shown on Figure 1. The reactor is a multiple-hearth furnace 2 m high and 0.7 m diameter, with six hearths. Heat transfer is provided through heating elements.

At the onset of an experiment wood chips are poured batchwise in a hopper that sits on top of the reactor. The hopper is equipped with a feeding device and is hermetically sealed. For the experiments reported, 6 to 15.4 kg of wood chips with a granulometry 1/4" to 1/2" Tyler Sieves were fed at a constant rate of 0.8 to 3.3 kg h^{-1}.

A mechanical vacuum pump removed the organic vapor and gas products from the reactor through a series of outlet manifolds set along the reactor cylinder. Each outlet was connected to a heat exchanger where the vapors were condensed and recovered as liquid into individual glass receivers. Cold tap water circulating on the shell side of the exchangers was used as cooling medium. The vapors from the heat exchange units were collected in a train of receivers that served as a secondary condensing unit. The first receiver was immersed in a bath of a water-ethylene glycol mixture. Receivers 2 and 3 were immersed in baths of dry ice-acetone. Receiver 4 was filled with glass wool at room temperature.

Pressure in the system was lower than 10.7 kPa (absolute) under steady-state conditions. The noncondensable gas was continuously pumped into a 500 L vessel that was set under vacuum at the beginning of the run.

The solid residue was directed toward the bottom of the reactor. The residual charcoal was received in a metallic jar installed on a load cell.

At time zero of the run, wood chips were fed in the preheated reactor. The heating plate temperatures increased from top to bottom of the reactor. A typical temperature profile was 200°C to 450°C. The radial temperature gradient for any heating plate was lower than 5°C during any single run.

The P.D.U. was attached to a central microprocessor that permitted simultaneous data acquisition and control of some 75 operating parameters (64 are recorded and 11 are controlled). Air leakage through the system was lower than 1.3×10^{-3} atm L s^{-1}. A list of recorded data as a function of time for a typical run is presented in Table 3.1 of the report.

Several photographs of the Process Development Unit equipment will be found in Appendix 1 of the report.

FIGURE 3.1 - SCHEMATIC OF VACUUM PYROLYSIS PROCESS DEVELOPMENT UNIT.

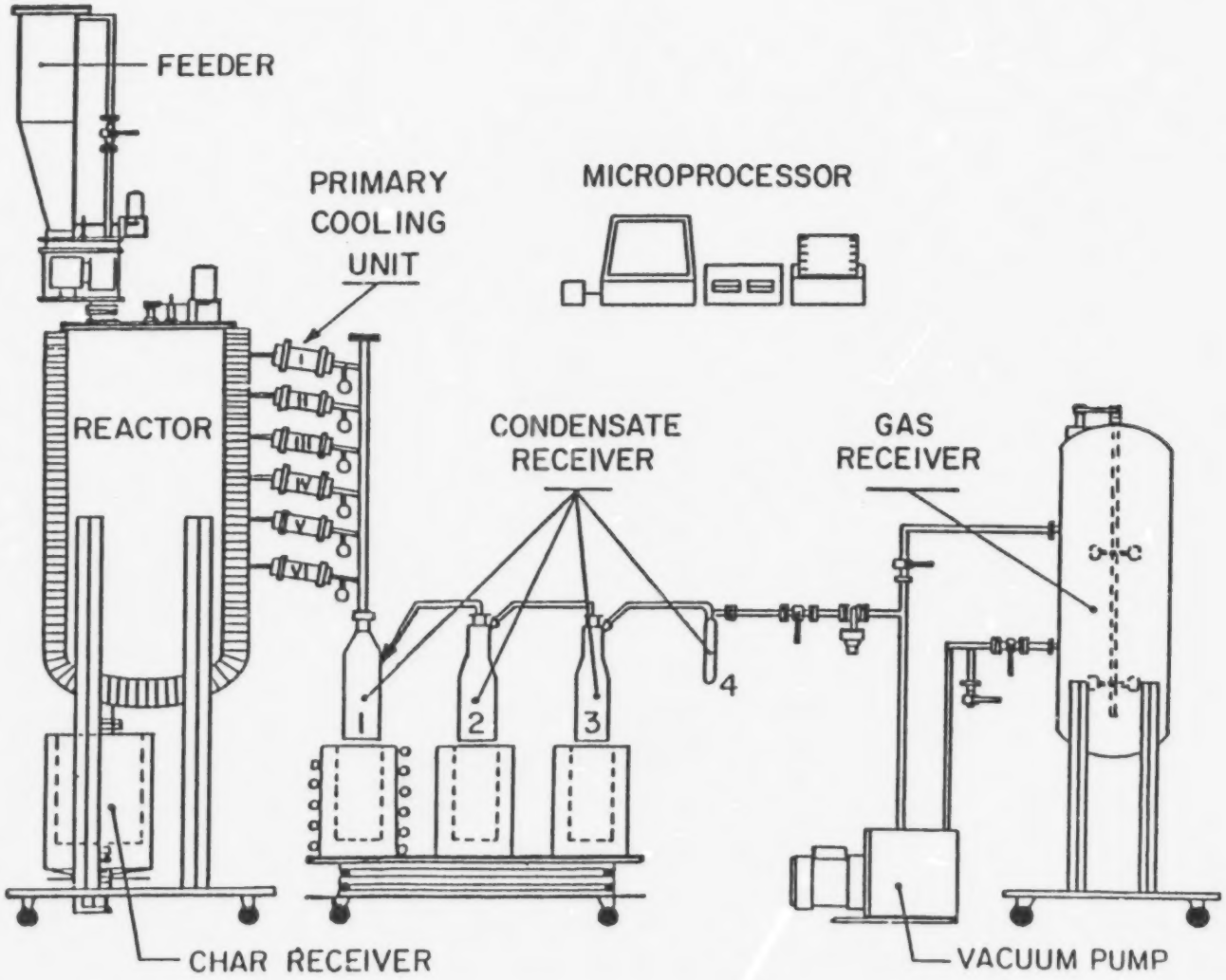


TABLE 3.1 - LIST OF RECORDED DATA AS A FUNCTION OF TIME

RECORDING #	RECORDED DATA
1-6	Hearth temperature I to VI
7-14	Temperatures of reactor wall (there are 8 of them)
15	Charcoal temperature at reactor outlet
16	Continuous weighing of wood charcoal produced
17	Continuous weighing of wood feedstock flowrate
18	Cooling temperature for secondary cooling unit (receiver #1)
19	Reactor pressure
20	Noncondensable gas pressure in gas tank
21-22	Differential on-line pressures
23	Electric voltage in
24-29	Temperature of heat tracers for gas outlets I to VI
30	Temperature of liquid condensate #3 (secondary cooling unit)
31	Box #1 offset
32	Box #1 reference (°C)
33-38	Temperature of gas and vapors from the reactor outlets (there are 6 of them)
39-44	Temperatures of gas and vapors at the inlets of the primary heat exchanger units (there are 6 of them)
45-50	Temperatures of gas and vapors at the outlets of the primary heat exchanger units (there are 6 of them)
51-56	Temperatures of water inlet for the primary heat exchanger units (there are 6 of them)
57-62	Temperatures of water outlet for the primary heat exchanger units (there are 6 of them)
63	Box #2 offset
64	Box #2 reference (°C)
65-74	Power consumed by heat tracer operation (there are 10 of them)
75	Total power consumed by the system

3.2 Materials Characterization

The experiments conducted on the P.D.U. were performed with Populus deltoides. The 8-year-old fast-growing poplar clone D-38 was planted in Brockville, Ontario. The sample was essentially all sapwood with no bark. It was shipped to our laboratories in the form of chips by Forintek Canada Corp., Ottawa. Its elemental composition was determined to be 48.2% C, 6.4% H, 45.3% O, 0.09% N, and 0.05% S. Its gross heating value was 19 507 kJ kg^{-1} with and average ash content of 0.6%. Moisture of the air-dry feedstock was determined to be 5.9%. The standard wood certificate is reproduced in Appendix 2 of this study.

The major products obtained from the vacuum pyrolysis of wood are in a solid, a liquid and a gaseous form. Each product phase was routinely analysed for its proximate and elemental composition and its calorific value. The standard procedures used are summarized in Table 3.2.

One major component contained in the pyrolytic liquors is acetic acid. Formic acid is another carboxylic acid detected in significant proportion. The procedures available in the literature for the determination of low-molecular-weight carboxylic acids are not really satisfactory, mainly because of the poor precision for the determination of formic acid. A new method based on the derivatization of acids (C_1 to C_7) with benzyl bromide was established and was successfully used. A capillary column gas chromatograph was

TABLE 3.2 - STANDARD PROCEDURES USED FOR THE CHEMICAL CHARACTERIZATION OF WOOD FEEDSTOCK, CHARCOAL AND PYROLYTIC LIQUORS

TEST	WOOD FEEDSTOCK	CHARCOAL	PYROLYTIC LIQUORS
Moisture	ASTM D2016	ASTM D1762	Karl Fischer
Ash	ASTM D1102	ASTM D1762	----
Volatile matter	Leco MAC 400	ASTM D1762	----
Calorific value	ASTM E711	ASTM D2015	ASTM D240
C, H, N	Perkin Elmer 240C	Perkin Elmer 240C	Perkin Elmer 240C
S	ASTM E775	ASTM D3177	ASTM D129

used. The quantitative analysis was performed by means of the internal standard method. Details of the procedure for the determination of low-molecular weight carboxylic acids in wood pyrolytic oil are presented in Appendix 3.

4- RESULTS AND DISCUSSION

4.1 Data reliability and relevance

Results related to the yields of the pyrolytic products and which are presented in this study have been accepted or rejected on the basis of predefined mass balance closure. Any run with a mass balance closure lower than 95% was rejected. As a consequence, the results regarding the yield and conversion of biomass during pyrolysis reactions are fairly reliable in the authors' opinion.

The energy data base can be criticized in view of the scant data obtained. The results which have been obtained so far are preliminary. For instance, the energy required for conducting the pyrolytic reactions is accurate within 10-20%. The energy balance around the reactor is incomplete, due to the absence of data for the mechanical pump energy requirement. The estimated overall heat transfer coefficient is not more accurate than 50%. However the calculated calorific value distribution among the pyrolytic products is fairly accurate in our opinion.

In general, the reported data are preliminary and more work is needed in order to ascertain their reliability with respect to the contemplated process implementation. Also, there are not enough data in this report to be able to answer questions like "What is the effect of process parameters on calorific value of char, oil and gas?", "What is the effect of mass flow rate on product distribution?" However this report represents one step in that direction.

4.2 Effect of pressure and temperature on product yields

Several runs have been conducted following the experimental procedure as described previously. The operating conditions used for these runs and the yield and mass balance results have been summarized in Table 4.1 of the report.

The data shown in Table 4.1 enabled us to draw some conclusions about the influence of temperature and pressure on the products yields. This is an important question to be answered since one of the objectives of the process is to maximize the quantity of oils from biomass.

Based on the observation of runs C015 and C023 conducted at almost identical pressure, it was found that a 25°C difference for the hearth temperatures, in the range of 425°C to 450°C, did not have

TABLE 4.1 - YIELDS AND MASS BALANCES FOR TYPICAL RUNS PERFORMED WITH THE P.D.U.

RUN #	TOTAL WEIGHT OF WOOD FEEDSTOCK (kg)	WOOD MOISTURE (% mt.)	AS-RECEIVED FEEDSTOCK MASS FLOWRATE (kg h^{-1})	REACTOR PRESSURE (kPa)	HEARTH #VI TEMPERATURE (°C)	YIELDS (kg/kg, wood organic basis) OILS	CHARCOAL	WATER	GAS	MASS BALANCE CLOSURE (%)
12	5.985	6.0	1.0	2.4	363	41.7	33.2	14.6	10.5	97.2
14	6.034	7.6	0.75	3.3	450	46.1	25.5	16.8	11.6	96.0
15	5.994	4.1	0.75	1.9	425	51.1	24.7	14.6	9.6	97.2
19	3.385	4.9	0.8	10.7	465	40.8	25.1	20.1	14.0	95.5
23	15.420	5.2	3.34	1.6	450	50.5	21.1	17.2	11.2	98.3

any significant effect upon oil yield. The yield of charcoal, however, decreased from 24.7% to 21.1% when operating at higher temperature. One conclusion which one can draw here is that a temperature of 450°C is optimal for the production of oils. This is also a straight extrapolation of past studies at the laboratory level.

At a reactor temperature above 450°C, the effect of temperature is much smaller than that of pressure. Such influence is remarkable when observing runs CO14 and CO23 at identical decomposition temperature. The oil yield is dramatically decreased when pressure increases from 1.6 to 3.3 kPa. This effect becomes even more evident when comparing runs CO19 and CO23, at similar decomposition temperature (the mass flow rate is an independant variable here). In this case, the oil yield dropped from 50.5% down to 40.8% when increasing pressure from 1.6 to 10.7 mm Hg. This drop (with a corresponding increase in charcoal of 4%) was also observed at the higher temperature condition, which is a strong indication that pressure is a much more important parameter than temperature around 450°C. One observes that the results for runs 12 and 19 have similar oil yields, which is explained by the wide difference between the pressure and temperature conditions used. These conditions are such that their influence on oil yields counterbalances, leading to almost identical oil yields.

It can be concluded from these results that the influence of temperature on the product distribution confirms that found at the

laboratory scale level. The role of pressure is more important than predicted at the bench scale level. One postulated reason for the discrepancy between these conclusions is the use of nitrogen as carrier gas (batch study) which at the same time artificially made the pressure in the systeme. No inert carrier gas was used with the P.D.U..

A general remark here is that although there are not many data points available, the latter are supported by excellent mass balances. Also, in the authors' opinion, these results are highly coherent from one experiment to the other.

Biomass pyrolysis is known to produce a high production of pyrolytic water. This water reduces the quality of the oil product. This problem was looked after during this study. The strategy used involved a separation, during the condensation, of the organic liquid phase product from the aqueous phase product. Section 4.7 of the report deals with this subject matter. As well the calorific values of the pyrolytic products are reported in section 4.6 of the study.

4.3 Energy required for conducting the pyrolysis reaction

One important objective of this contract work was to improve our knowledge of the thermal efficiency and energy balance for the vacuum pyrolysis reactions. One unknown was the energy required for conducting the pyrolytic reactions. This problem has been

discussed and solved as shown below. The energy dissipated when cooling the vapor products at the outlets of the multiple hearth furnace (primary stage) has been determined as well. Another important objective of this study was to estimate the overall heat transfer coefficient, which in turn is needed to optimize the design of the reactor. The preliminary calculations leading to the U coefficient are presented in this report.

The energy balance around the reactor can be assessed following a calculation of the total energy required for conducting the pyrolytic reactions. This was determined by comparing the total energy lost to the atmosphere before and after the main run (blank runs) with the energy consumed during the run itself (wood fed). Such values have been computed after integration of the power versus time function (see Appendix 4 for further calculation details). The data obtained are summarized in Table 4.2.

The most reliable data in Table 4.2 are related to experiment C023, mainly because a more significant increment was obtained between background energy (heat loss) and reaction energy. As a result, the total energy required for conducting the vacuum pyrolysis reaction was found to be 615 kJ kg^{-1} of anhydrous wood. The accuracy of this last result is estimated to be of the order of 10 to 20%.

TABLE 4.2 - ELECTRICAL ENERGY REQUIRED FOR CONDUCTING THE PYROLYTIC REACTIONS

RUN #	FEEDING TIME (h)	CONSUMED POWER (W) BLANK BEFORE RUN	TEST RUN	BLANK AFTER RUN	HEAT REQUIRED ($kJ\ kg^{-1}$) AS-RECEIVED WOOD	ANHYDROUS WOOD
14	8.0	n.d.	3750	3747	(b)	(b)
15	8.0	n.d.	1919	1820[a]	711.6	644.6
19	n.d.	1532	1621	1550	519.1	427.0
23	4.6	1649	2230	1639	699.1	615.3

n.d.: not determined
(a) graphical determination (as opposed to numerical determination)
(b) no significative value could be calculated in this case

4.4 Energy removed at the primary cooling stage

A great deal of the organic liquid products are recovered at the primary cooling stage of the P.D.U. (see Figure 3.1). Six shell and tube heat exchangers with cool water circulating on the shell side have been used. The cooling water flowrate was carefully monitored and temperatures for inlet and outlet water, inlet and outlet vapor product and outlet liquid product were recorded. The calculations leading to the determination of the total energy removed were conducted for run C023 (the run with the most extensive data) where cooling water was circulated at 50°C constant. The energy removed when condensing and cooling the vapor products at the primary cooling stage was determined to be 452 kJ kg^{-1} of anhydrous wood. The kind of equipment used didn't enable us to determine the energy removed at the secondary cooling stage ("condensate receivers" in Figure 3.1) during the work. However, the latter is assumed to be small in comparison with the other one.

Another goal was to determine the overall heat transfer coefficient (U_c) for the shell and tube heat exchangers. This objective wasn't achieved due to improper gas temperature measurement. The source of the problem was found to be the type of thermocouple used (ungrounded, type J). Under the vacuum operating conditions used, the heat exchanged by convection with the gas phase is smaller than the heat exchanged through conduction with the surroundings. As a consequence, the recorded temperature is not

the true one. This is referred to as the "cooling fin effect" [cf. Bird, R.B., Stewart, W.E., and Lightfoot, E.N. "Transport phenomena" John Wiley & Sons Inc. pp. 288-291. (1960)].

Such effect is counterbalanced when using an exposed thermocouple with no shield on the tip and where a small spherical and metallic band is added. Such a device reduces the possibility of conduction effect by both increasing the mass and the thermocouple surface exposed to the convection effect. Figures 4.1 and 4.2 illustrate the modifications that are needed.

Under the operating conditions used, the error attributed to the radiation and gas friction was assumed to be negligible.

4.5 Energy balance around the reactor

The reliability of the energy data base found in previous sections 4.3 (energy required for conducting the pyrolysis) and 4.4 (energy removed at the primary cooling stage) was tested by conducting an energy balance around the reactor. This was done for run C023 at a reference temperature of 50°C. In such calculation the heat capacity of wood was assumed to be 0.5 cal g^{-1} $°C^{-1}$, and that of wood charcoal 0.246 cal g^{-1} $°C^{-1}$, throughout the temperature range considered. The calculations are summarized in Figure 4.3.

At 50°C, the total energy into the system is the electric energy consumed. This energy can be expressed in kJ on an hourly basis

FIGURE 4.1 - THERMOCOUPLE INITIALLY USED FOR GAS TEMPERATURE MEASUREMENT IN VACUUM

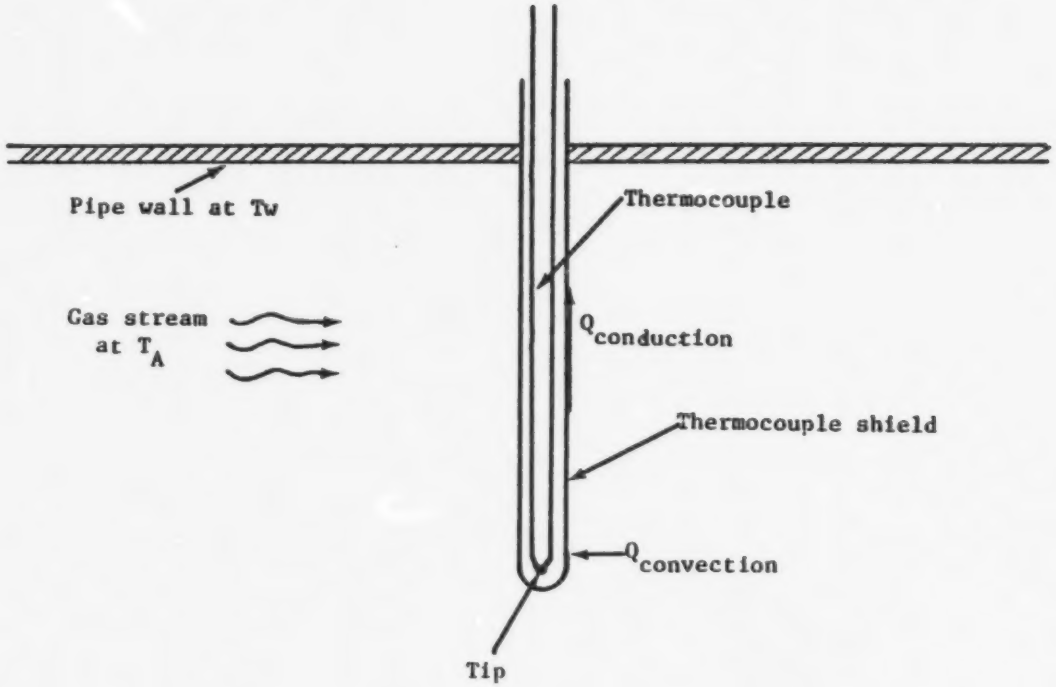


FIGURE 4.2 - MODIFIED THERMOCOUPLE REQUIRED FOR GAS TEMPERATURE MEASUREMENT IN VACUUM

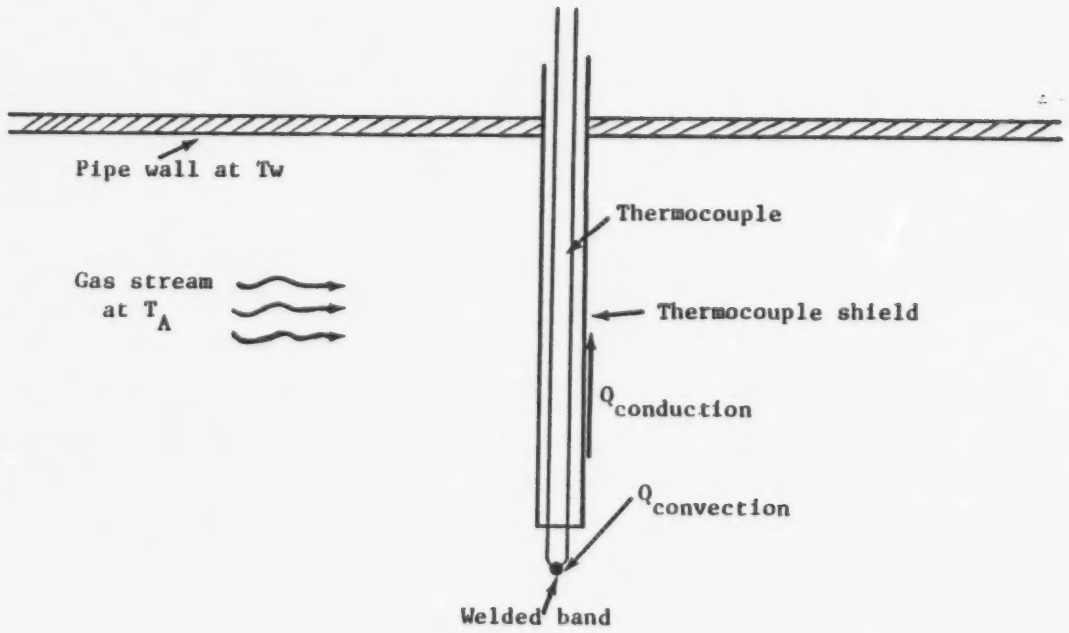
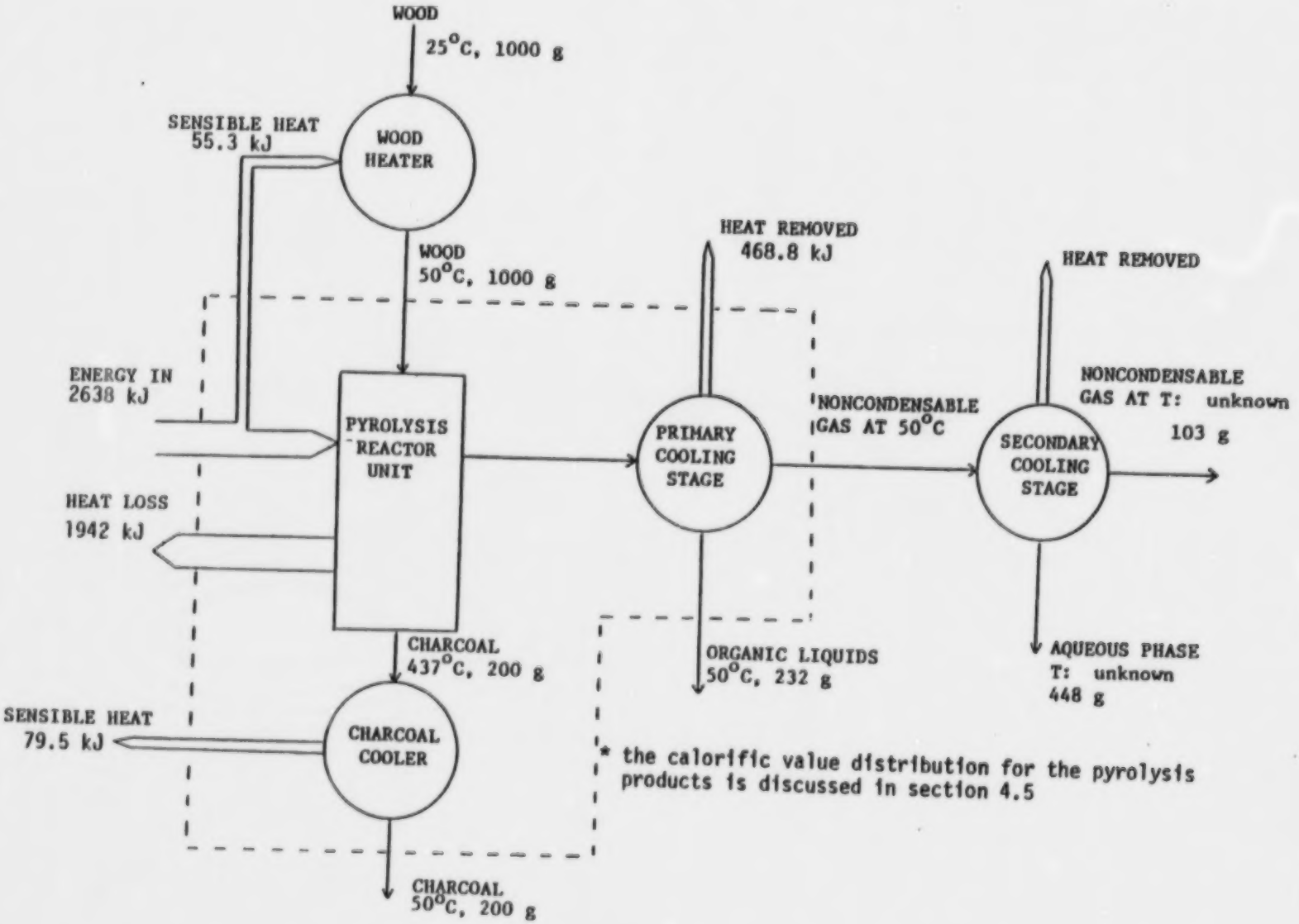


FIGURE 4.3 - ENERGY BALANCE AROUND THE PYROLYSIS REACTOR*



* the calorific value distribution for the pyrolysis products is discussed in section 4.5

starting from the average data in Table 4.2. The energy out of the system is the sensible energy removed from the pyrolytic oils at the primary cooling stage plus that removed from the hot charcoal. Part of the energy in is used to heat up the wood feedstock from room temperature to the reference point (°50C). The sensible heat contained in the gas phase at 50°C is nil since this temperature was chosen as reference. The energy balance at the outlet of the primary cooling stage at 50°C is as follows:

Total energy in	:	2638 kJ
Energy out	:	1942 kJ (heat loss)
		55.3 kJ (wood from 25 to 50°C)
		468.8 kJ (primary cooling stage)
		79.5 kJ (cooling of charcoal)
Total	:	2545.6 kJ
Balance	:	$\frac{2638 - 2545.6}{2638} = 3.5\%$

It can be concluded from these calculations that the energy data base obtained so far is fairly reliable.

It has not been possible to estimate the thermal efficiency of the whole process during this contract work. However an estimate of the calorific value distribution for the solid, liquid and gas pyrolytic products was attempted.

It was concluded that the original wood feedstock heating value is equally distributed between the organic liquid and residual solid products. The noncondensable gas phase product represents only 5.5% of the total initial wood calorific value. Such calculations did not take into account the sensible heat of any products. The total calorific value contained in the pyrolytic products equals 84.5% that of the raw material. The calorific value of the oil on the average is 15 635 kJ kg^{-1} and that of wood charcoal is 29 230 kJ kg^{-1}.

4.6 Heat transfer phenomena during pyrolysis

One unknown is still the rate at which heat is being transferred to wood during pyrolysis reactions. Heat can be transferred by conduction, by radiation and by convection. It is thought that convection actually plays a minor role under the reduced pressure conditions used. The role of radiation increases as the reactor temperature goes up, particularly at temperatures higher than 500°C. It has not been possible to differentiate between heat transferred by conduction and heat transferred by radiation in this study.

An understanding of the overall heat transfer phenomena was attempted. An overall heat transfer coefficient (U) was calculated based on the values obtained for the reaction heat requirements (see section 4.3) and based also on the wood feedstock inlet temperature and the charcoal outlet temperatures, as well as on

reactor temperature operating conditions. Again, run C023 was chosen for this calculation since it was felt to be the experiment with the most reliable data. It was estimated that 30% only of the total available surface on top of each hearth was covered with solid material. This value was determined following a cold run of the reactor with raw wood chips (1/4"-1/2" Tyler Sieves). There is experimental evidence, however, that the effective surface area used for heat transfer is smaller due to the shrinking of the wood particles during their conversion into charcoal. As a consequence, the calculated U value below is underestimated.

The U can be estimated from the relation

$$q = U\ A\ (\Delta T)_{ln}$$

A = surface area used for heat transfer (m^2)

q = rate of energy being transferred from the reactor to the wood particle ($kJ\ h^{-1}$)

$(\Delta T)_{ln}$ = temperature driving force (°C). This will be expressed as the logarithmic mean.

U = overall heat transfer coefficient ($kJ\ h^{-1}\ m^{-2}\ °C^{-1}$)

Surface area (A):

There are 6 hearths, 21 inches in diameter. The total surface for the reactor is:

$$\frac{\pi}{4}\ (21\ in)^2 \times 6 = 2078\ in^2$$

Only 30% of the surface is used for transferring heat to wood particles, or 623 in² (= 0.40 m²).

Rate of heat transfer (q):

The total amount of heat being transferred corresponds to the heat required for conducting the pyrolysis reaction. This was calculated in section 4.3. This value is 699 kJ kg^{-1} of as-received wood (the initial wood moisture content must be included for these calculations). At a mass rate of 3.34 kg h^{-1}, the rate of heat transfer is:

$$q = \frac{3.34 \text{ kg}}{\text{h}} \left| \frac{699 \text{ kJ}}{\text{kg}} \right. = 2334.7 \text{ kJ h}^{-1}$$

Driving force $(\Delta T)_{\ell n}$ *:*

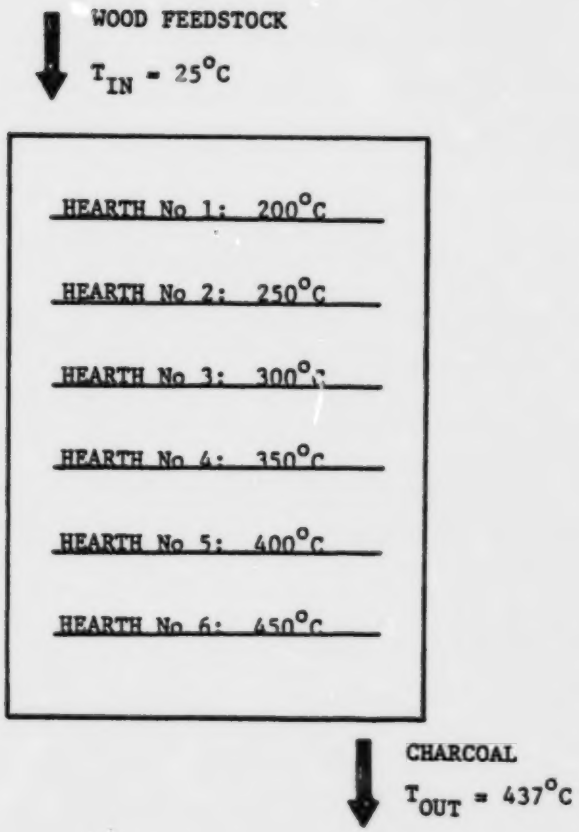
The driving force for heat transfer is the logarithmic temperature differential between inlet feedstock temperature and reactor inlet temperature on the one hand, and the outlet charcoal temperature and reactor outlet temperature on the other hand. A schematic illustrates the temperature configuration in Figure 4.4 $(\Delta T)_{\ell n}$ is calcualted as follows:

$$\Delta T_{\ell n} = \frac{\Delta T_I - \Delta T_{II}}{\ell n \frac{\Delta T_I}{\Delta T_{II}}} = \frac{(200 - 25) - (450 - 437)}{\ell n \frac{(200 - 25)}{(450 - 437)}} = 62^{o}C$$

$$U = \frac{q}{A \Delta T_{\ell n}} = \frac{2334.7 \text{ kJ}}{\text{h}} \left| \frac{}{0.4 \text{ m}^2} \right| \frac{}{62^{o}C}$$

$$\approx 92 \text{ kJ h}^{-1} \text{ m}^{-2} \text{ }^{o}C^{-1}$$

FIGURE 4.4 - TYPICAL TEMPERATURE PROFILE WITHIN AND AROUND THE MULTIPLE HEARTH FURNACE



Discussion about U coefficient

The overall heat transfer coefficient concept is mainly used for heat exchangers where there are no phase changes in the circulating fluid materials. In some cases it has been used for simulating cement kiln operation at high temperatures. The concept is useful when comparing processes with each other.

Obviously, the multiple hearth furnace used in this study isn't a simple heat exchange unit. The U concept has been introduced here strictly for comparison purposes. The model can be improved, (a) by better insulating the reactor, thus reducing the heat loss to the atmosphere, and (b) by increasing the feedstock flowrate in order to ultimately cover the whole hearth surface available.

The U value obtained is in range with other data available in the literature for the carbonization in multiple hearth furnace of materials similar to wood and charcoal. (Ref: Perry, R.H. and C.H. Chilton, Editors, Chemical Engineer's Handbook, McGraw-Hill Book Company, 5th Edition, New York, 1973. Chapters 3 and 11).

4.7 Wood oil analysis. Selectivity during the condensation stages.

An analysis of the wood oil samples produced at the different cooling sections of the P.D.U. was conducted. The samples were

analyzed for their contents of water, acetic acid and formic acid. These three compounds are major products found in wood pyrolytic liquors. One objective of such analyses was to estimate the degree of selectivity with which the liquid products can be condensed and separated. This question has been addressed during this work by first considering the three major compounds cited above, as opposed to spending time making analyses of other minor carboxylic acid components. The data obtained are summarized in Table 4.3 for run C019 and in Table 4.4 for run C023.

The preliminary results show that it is possible to separate the bulk of the aqueous phase from the organic liquid phase. The degree of separation between the two phases is influenced by both the reactor pressure and the cooling temperature. For the two experiments herein reported, the reactor pressure was higher for run C019 (as opposed to run C023) and cooling temperature was lower.

The extent of the selectivity with which the oils are recovered at the different outlets of the primary cooling unit also depends on the pressure and temperature of the heat exchanger unit. So far it seems that the process has potential to achieve the separation of organic compounds with a certain degree of selectivity.

TABLE 4.3 - WATER, FORMIC AND ACETIC ACID CONTENTS OF WOOD OIL AND AQUEOUS PHASE SAMPLES CONDENSED AT DIFFERENT STAGES OF THE P.D.U. RESULTS FOR RUN C019.

	ACETIC ACID (g)	FORMIC ACID (g)	TOTAL WATER (g)
PRIMARY COOLING UNIT			
Condenser I	38.23	8.17	208.2
" II	27.31	7.24	65.1
" III	20.78	7.25	59.2
" IV	10.61	5.95	40.3
" V	2.52	1.72	16.9
" VI	1.37	0.54	6.9
SECONDARY COOLING UNIT			
Receiver 1	18.03	2.92	394.3
" 2	2.15	0.35	35.7
" 3 + 4	1.15	0.12	6.4
TOTAL (Primary + Secondary Units)	112.15	34.26	833
Yield (% w/w, wood organic basis)	3.81	1.07	

TABLE 4.4 - WATER, FORMIC AND ACETIC ACID CONTENTS OF WOOD OIL AND AQUEOUS PHASE SAMPLES CONDENSED AT DIFFERENT STAGES OF THE P.D.U. RESULTS FOR RUN CO23.

	ACETIC ACID (g)	FORMIC ACID (g)	TOTAL WATER (g)
PRIMARY COOLING UNIT			
Condenser I	13.93	5.32	16.19
" II	14.14	4.34	19.15
" III	22.55	8.22	26.63
" IV	19.93	22.94	40.83
" V	14.99	29.66	31.81
" VI	3.78	8.63	5.99
SECONDARY COOLING UNIT			
Receiver 1	295.22	215.18	718.11
" 2	278.32	153.68	2017.00
" 3 + 4	55.08	24.31	280.51
TOTAL (Primary + Secondary Units)	717.94	472.28	3156.28
Yield (% w/w, wood organic basis)	4.94	3.25	

CONCLUSIONS

Vacuum pyrolysis has been confirmed as a promising approach for the production of high yields of oils and chemicals from biomass. A thermal decomposition temperature in the range of 425 to 450°C and an as low pressure as possible is optimal for the production and recovery of oils. Oil yields of 50 kg/100 kg of anhydrous wood have been obtained; the calorific value of this oil is about 15 600 kJ kg^{-1}. This oil is a source of valuable chemical compounds like low-molecular-weight carboxylic acids but it is not possible at this stage of the work to determine whether it is possible to produce and selectively recover such chemicals.

The required energy for conducting the pyrolytic reactions has been determined to be 615 kJ kg^{-1} of anhydrous wood. The overall heat transfer coefficient for the reactor has been estimated at 92 kJ h^{-1} m^{-2} $°C^{-1}$. Heat removed at the primary cooling stage to recover the organic liquids has been found to be 452 kJ kg^{-1} of anhydrous wood.

More work is needed to complete this part of the engineering study of the vacuum pyrolysis process. This includes a better understanding of the heat transfer phenomena in the reactor; more data are also needed in order to determine the overall thermal efficiency of the process, and the overall heat transfer coefficient for the heat exchange units (cooling system). More data should be obtained in order to correlate various independent variables (e.g., mass flow rate, pressure, temperature...) and product distribution and characterization.

RECOMMANDATIONS

At the fundamental level, a better study of heat transfer phenomena which occur in the reactor is needed. The role of radiation should be given particular consideration as opposed to the role of heat transferred by conduction. Also, it is not clear at the present time whether the multiple hearth furnace vacuum pyrolysis reactor can operate as a "distillation column" in order to obtain different grades of liquid products at the reactor outlets. A better study of 1) the mass flowrate and residence time distribution of the solid particles and vapors inside the reactor, 2), the mode of condensation and 3), the nature of gas and vapors to be condensed, would ultimately result in an improved selectivity of the organic compounds.

Apart from the two minor points mentined above, the basic engineering data for the vacuum pyrolysis concept are now such that the process can be evaluated at the pilot stage with a continuous feeding rate in the range of 100 to 200 kg h^{-1} of wood chips.

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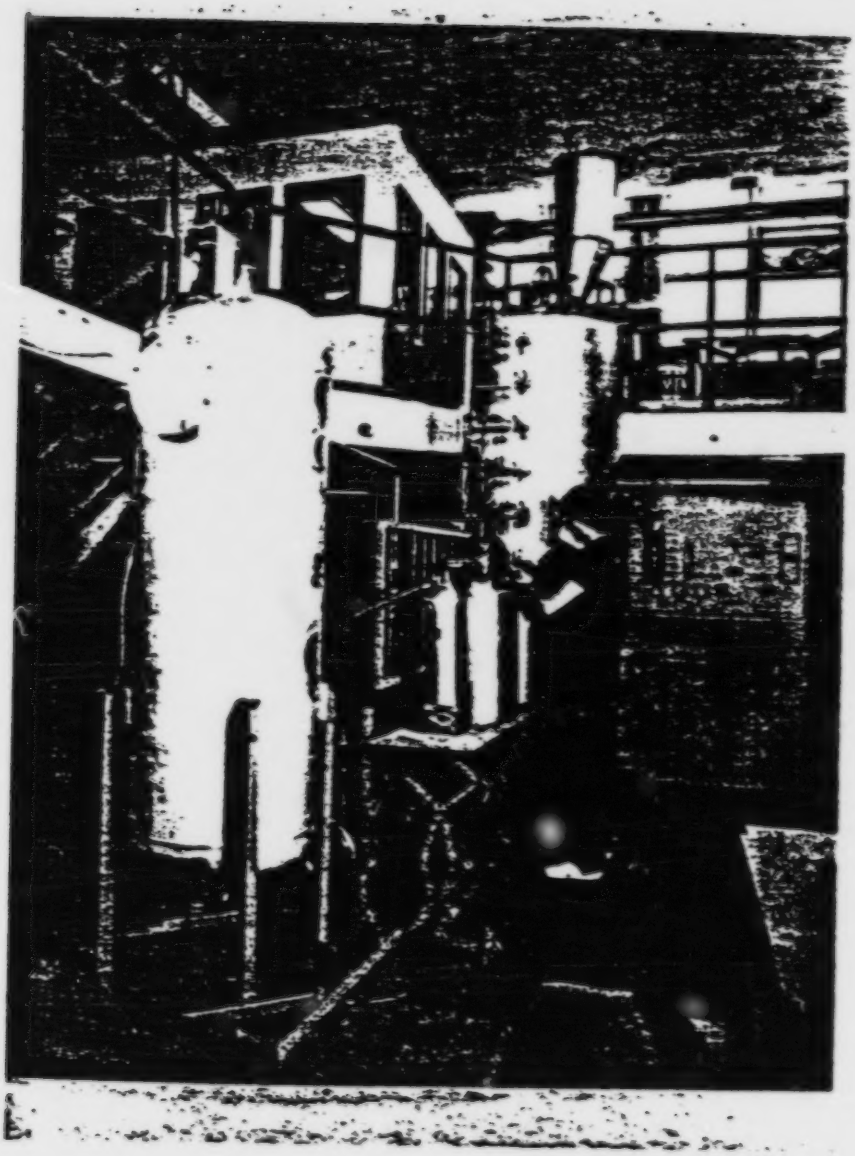
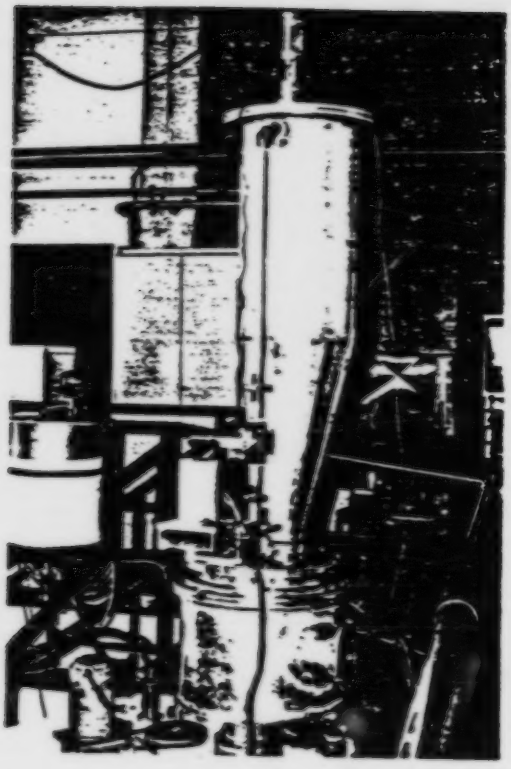
APPENDICES

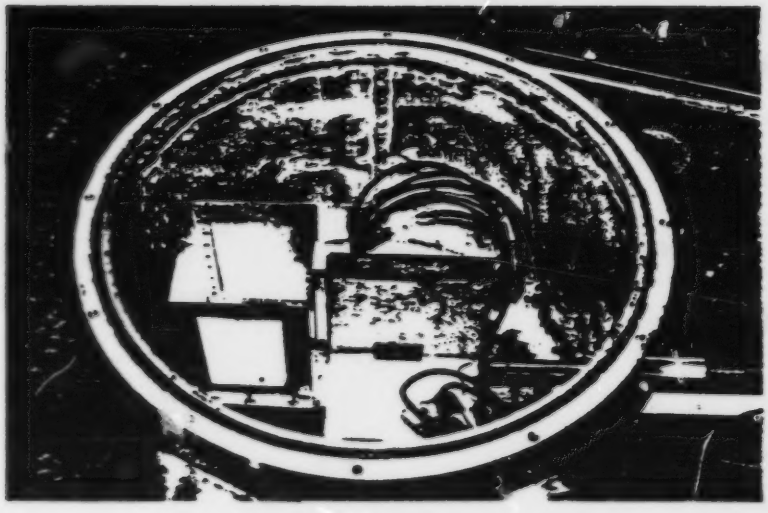


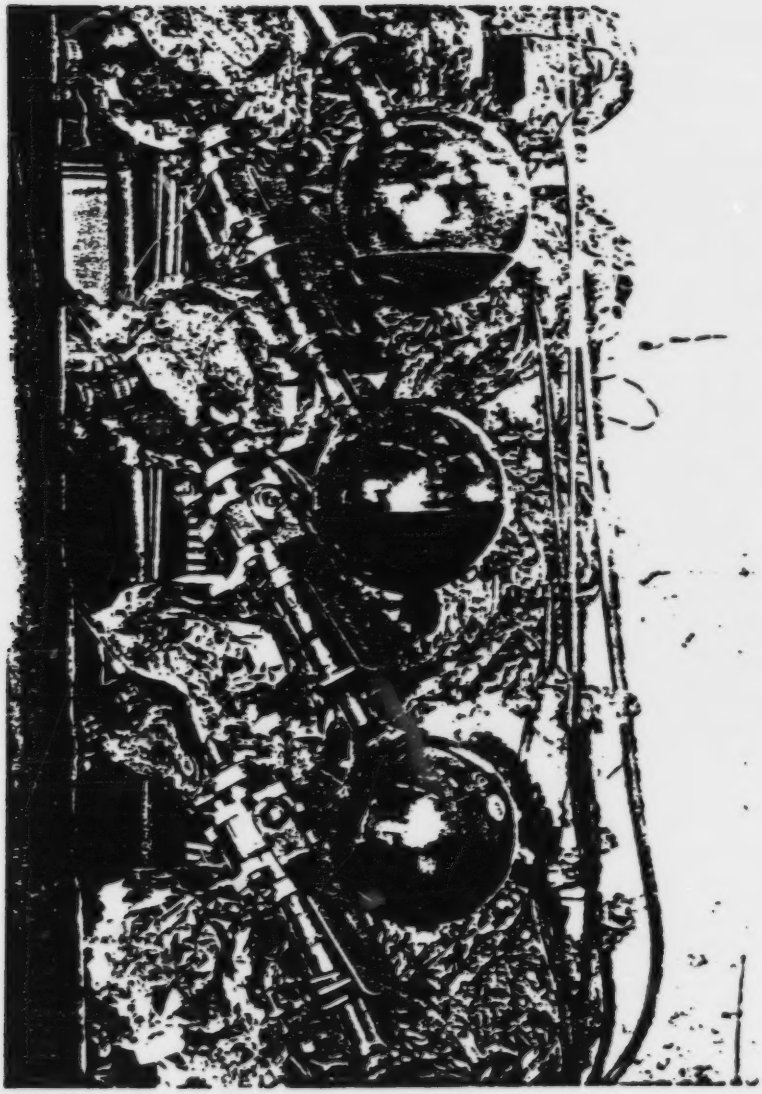
Process Development Unit for vacuum pyrolysis.



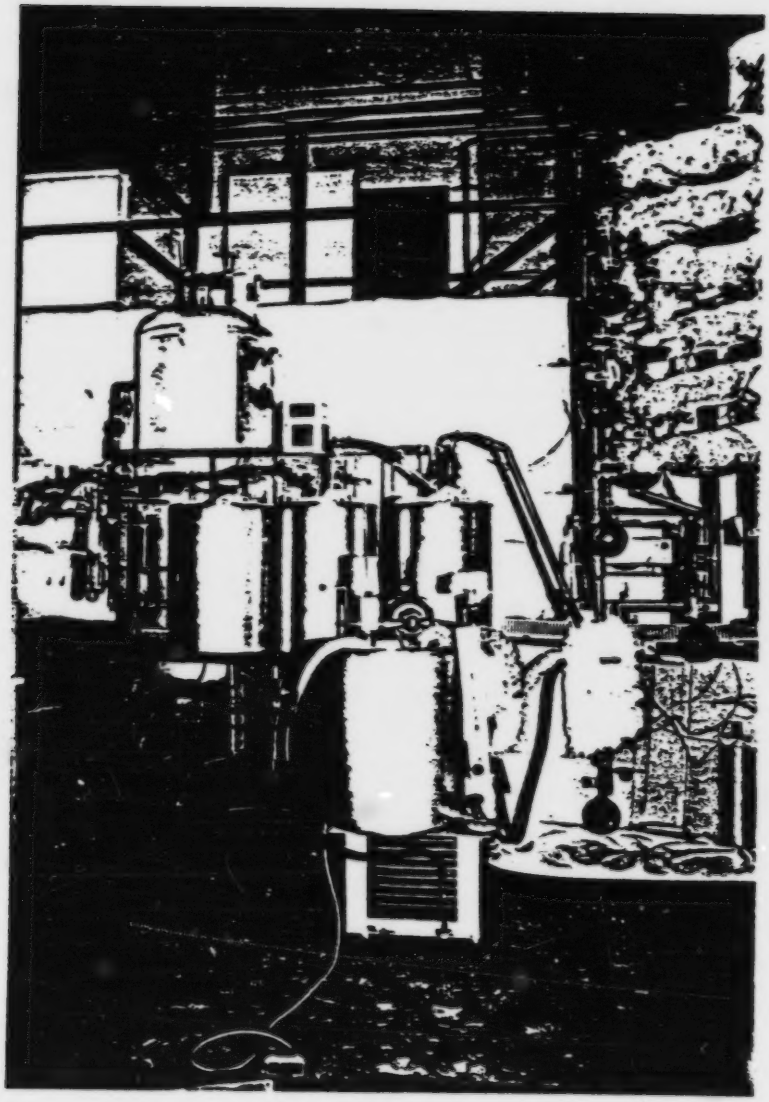
Wood chips feeding system.

Inside view of load cell connected to the wood chip trap (bottom of feed hopper).

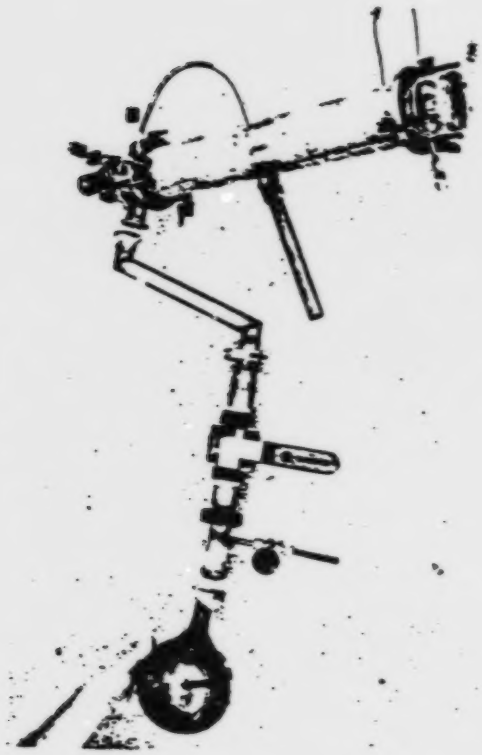




Wood oils condensed in the primary cooling unit.

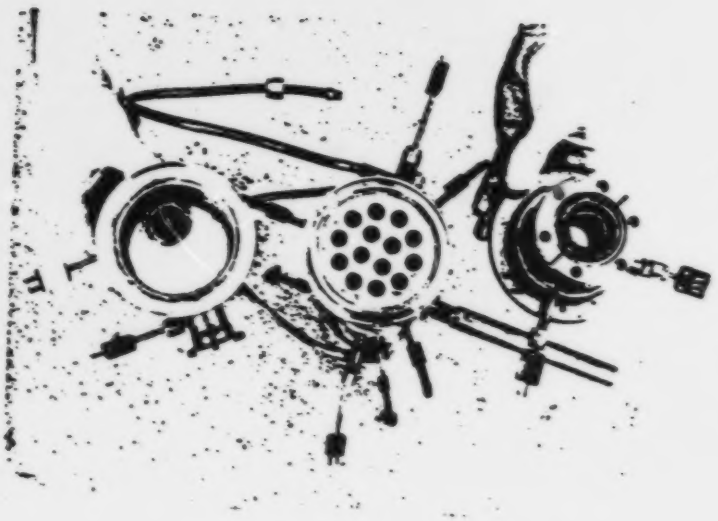


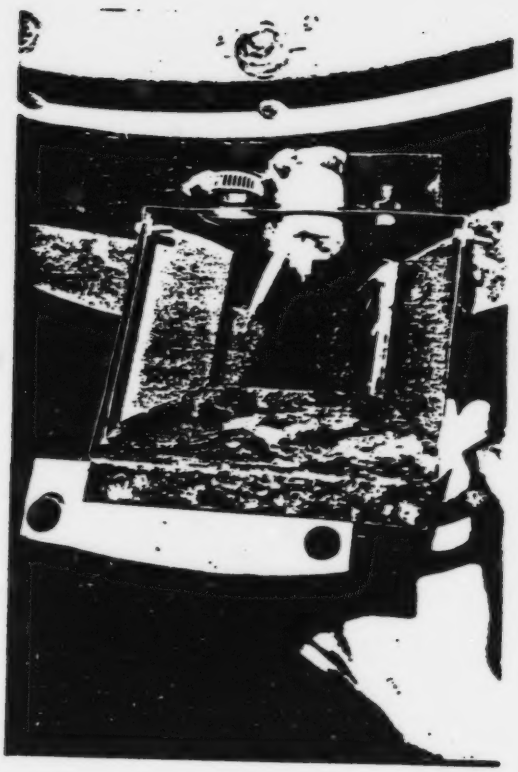
Primary and secondary cooling unit system and gas receiver.



Shell and tube heat exchanger, valve and flask of primary cooling unit.

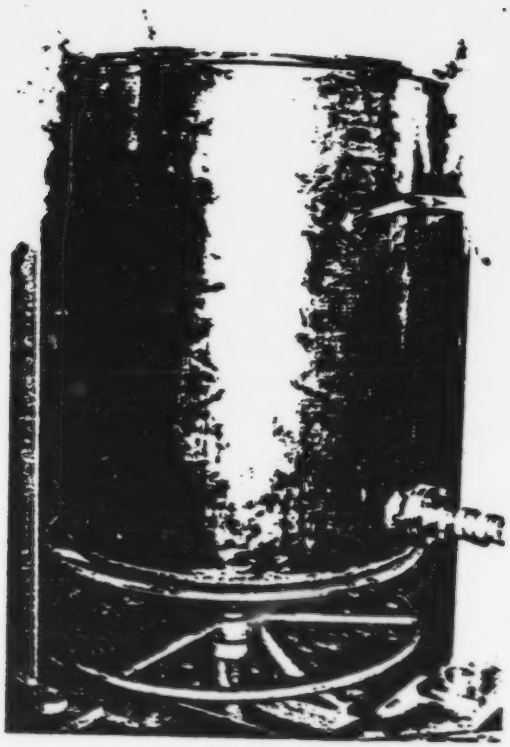
Inside view of shell and tube heat exchanger.





Wood charcoal trap and thermocouple for determination of the final charcoal temperature.

Wood charcoal receiver unit.



APPENDIX 2

STANDARD WOOD CERTIFICATE

The Sample is defined according to the criteria identified by G.M. Barton, 1984.

1.	Species	Populus Deltoides - Clone D-38
2.	Site	Brockville, Ontario. 75.40°W, 44.35°N. 100 m. ASL.
3.	Sampled	May 8, 1984.
4.	Vertical Distance of Samples	Discs for SG measurement were taken at a height 1m and had a diameter of 10 - 15 cm. The grab samples for chemical analysis were of the final homogenized dried sample of 2000 kg.
5.	Diameter of Cross-section	= 10 - 15 cm.
6.	Thickness of Cross-section	= 2 - 3 cm
7.	Planted Harvested Age	April 1976 May 1984 8 years
8.	Heartwood	Nil

9. Sample essentially all sapwood - no bark.

10. The sample is composed of clear fast growing poplar which will tend to have more juvenile wood characteristics than mature slowly grown species.

11.	Sample Storage	After felling the harvested trees were transported to Ottawa and debarked. The cleaned bolts were chipped approximately one month later. The chips were then air dried to 6% moisture, sieved sampled and polythene bagged in 20 kg lots and stored in cardboard shipping containers in a dry area at ambient temperature.
12.	Moisture Content	As received = 50% total weight/basis Grab samples = 6 - 8% total weight/basis

/2

Analysis

3 separate analyses were carried out and are listed in NRCC (to be announced). The recommended values are:

Solid Wood Basic Specific Gravity	0.35
Higher Heating Value	19.5 MJ/g
Ash Content	0.61 + 0.047% at 1σ (TAPPI T211)

Ash Constituents % of Dry Ash Weight (Standard Deviation)

Ca	K	Mg	P	Na
19.27(2.49)	18.0(1.30)	4.28(0.23)	2.16(0.15)	1.25

Fe	Zn	Si	Al	Mn	Pb	Cu	B
0.29	0.21	0.05	0.06	0.07	0.12	0.10	0.05

Analysis by Atomic Absorption.

Sequential Extractives Content

Ethanol/Benzene %	1.78 (0.29)
Ethanol %	0.22
Water %	1.24
Total	3.24

TAPPI - T222 0574

Constituents		Elemental Analysis	
Klason Lignin	21.52%(0.81)	C	48.2
Soluble Lignin	2.7%	H	6.4
	24.2%	O	45.3
		N	0.09
α Cellulose	43.30%(0.97)	S	0.05
Hemicellulose	32.70%		
Pentosan (single analysis)	19.4%		

"STANDARD WOOD CERTIFICATE"

NOTE This is a preliminary document and will be revised and issued with a forthcoming NRCC report embodying all of the background to the sample. RPO 6/02/85

APPENDIX 3

DETERMINATION OF LOW MOLECULAR WEIGHT CARBOXYLIC ACIDS IN WOOD PYROLYTIC OIL

A method for quantitative and qualitative analysis of low molecular weight carboxylic acids in wood pyrolytic oil is developed. The method is based on conversion of the acids into their benzylesters which is followed by capillary gas chromatographic analysis.

METHOD

Apparatus

1) Capillary column (DB1 or DB5) gas chromatograph (GC) with flame ionization detector and integrator.

2) pH meter.

Reagents

Tetra-n-butylammonium hydroxide solution, 40% in methanol (TBA-OH).

Prepare a methanolic solution (30.8 $mmol_3 dm^{-3}$) by dissolving 2 g of TBA-OH (40%) in 100 cm^3 methanol

Benzyl bromide

Prepare a solution of 60 mmol dm^{-3} of benzyl bromide in the GC-grade acetone by dissolving 513 mg of benzyl bromide in 50 cm^3 acetone.

Preparation of the benzyl bromide solution should be made in fume hood and should be avoid of any contact with skin and avoid of inhalation. Store the solution in the fridge.

n-Octanoic acid

Carefully prepare a methanolic solution of 80 mg purified n-octanoic acid in 100 cm^3 methanol.

Procedure

Carefully and accurately transfer "m" mg of the tar (preferably ~40 mg) into 25 ml flask and add 0.5 ml of the standard n-octanoic acid solution and small volume of distilled methanol in order to obtain enough liquid for the pH meter's glass electrode. Carefully neutralize the sample with TBA-OH solution to pH of 9.00 (ν cm^3).

Since neutralization of the various acidic compouds in the tar is a slow reaction, therefore, allow enough time in order to achieve a stable PH. Transfer the neutralized tar mixture into a large volume flask ($\sim 250\ cm^3$) and carefully evaporate off the methanol in rotary evaporator (no high vacuum is required).

Add 1/2 $\nu\ cm^3$ (will be $\sim 2.5 - 3\ cm^3$) benzyl bromide solution to the dried mixture and allow the reaction mixture to stand while stirring for overnight.

Purification

Carefully evaporate off the acetone in the rotary evaporator to near dryness (avoid of using water bath) and then dissolve the mixture in about 50 cm^3 distilled petroleum ether (40-60°C b.p.) or distilled n-pentane and separate the pentane phase analyse by GC and calculate percentage of the acids in the tar using appropriate response factors which are shown in Table 1.

Since one mole of acid produces one mole of benzyl derivative, therefore, the following equation may be used to compute the acid percentages.

$$C_x = \frac{f_x \cdot m_i \cdot A_x \cdot M_x \cdot \bar{M_i}}{A_i \cdot \bar{M_x} \cdot m \cdot M_i} \quad 100$$

f_x = Relative response factor of the acid derivative

m_i = mg weight of the internal acid

A_x = GC peak area of the acid derivative

$\bar{M_x}$ = Molecular weight of the acid derivative

$\bar{M_i}$ = Molecular weight of the internal acid derivative

A_i = GC peak area of the internal acid derivative

M_x = Molecular weight of the acid

m = mg weight of the tar + internal standard

M_i = Molecular weight of the internal standard

3.

Gas chromatographic condition

Initial temperature : 50°C
Time 1 = 4 min

Rate = 10°C min^{-1}

Final temperature : 290°C
Time 2 = 10 min

Injection temperature: 295°C
FID temperature : 300°C

Table 1: Relative response factors for esters of carboxylic acids C_1 - C_8

Benzyl derivatives of	M.W.	Response factors experiment						Average
		1	2	3	4	5	6	
acid formic	136	1.83	1.91	1.80	1.84	1.83	1.88	1.85
" acetic	150	1.06	1.09	1.12	1.09	1.10	1.08	1.10
" propionic	164	1.02	1.04	1.08	1.04	—	—	1.05
" butyric	178	0.93	0.99	1.03	1.01	—	—	1.00
" pentanoic	192	1.00	1.06	1.03	1.02	—	—	1.01
" hexanoic	206	1.00	1.00	1.00	1.00	1.00	0.97	1.00
" heptanoic	220	1.00	1.00	1.00	1.00	1.01	0.99	1.00
" octanoic	234	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Calibration

Since there are significant differences in their behaviour in FID detector, benzyl esters of carboxylic acids (C_1 to C_8) were prepared and their relative response factors to benzyl octanoate were measured.

Preparation of the samples

Measure 1 mmole of each acids (C_1 to C_8) and dissolve them in 100 cm^3 distilled methanol. Transfer 3 cm^3 of the mixture into a 25 cm^3 flask and neutralize with TBA-OH solution (ν cm^3) to PH = 9.0. Dry the solution as mentioned before and then add 1/2 ν cm^3 solution of benzyl bromide and stir it for overnight. Evaporate off the acetone and dissolve it in about 25 cm^3 distilled petroleum ether or distilled n-pentane. Repeat this experiment for five times and store a dilute solution of each mixtures in the fridge.

Analysis

Inject 0.5 $\mu\ell$ of the samples into GC and calculate the the response factors relative to n-octanoic acid derivative as below and report average response factor for the each acid derivatives.

$$f_x = \frac{C_x A_I}{C_I A_x}$$

f_x = Relative response factor of acid ester to n-octanoic acid ester derivative

C_x = mg acid ester

C_I = mg acid octanoic ester

A_x = Acid ester peak area

A_I = Octanoic acid ester peak area

APPENDIX 4

DEVELOPMENT OF A BIOMASS VACUUM PYROLYSIS PROCESS FOR THE PRODUCTION OF LIQUID FUELS AND CHEMICALS

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ABSTRACT

A process is described whereby oils and chemicals are produced on a semi-continuous basis by thermal decomposition of aspen poplar wood chips under a reduced pressure. The reactor is a multiple hearth furnace, with six hearths being electrically heated. It's dimensions are 2m high by 0,7m in diameter. The vaper and gas products are continuously withdrawn, separated from the solid residues and condensed at six outlet sections of the reactor.

Organic liquid yields close to 30% by weight are obtained. Some characteristics of the liquid and solid products are reported. Water was found to play a major role in the corrosion activity of the pyrolytic oils. Heat required for conducting the pyrolytic reactions under vacuum was found to be very small as compared to the calorific value of the raw material.

The potential industrial implementation of the vacuum pyrolysis concept will be discussed, both in its current mode of operation for the direct production of oils and chemicals, and for the possible production of upgraded liquid fuels and chemicals.

DEVELOPMENT OF A BIOMASS VACUUM PYROLYSIS PROCESS FOR THE PRODUCTION OF LIQUID FUELS AND CHEMICALS

INTRODUCTION

Laboratory scale studies conducted at the Université de Sherbrooke have led to the conclusion that thermal decomposition under reduced pressure was an attractive approach for the conversion of biomass into chemicals and fuel products (5, 7). The development of data base for continuous process resulted in the design, construction and operation of a multiple hearth furnace Process Development Unit (P.D.U.) for the vacuum pyrolysis of wood chips, the details of which have been reported elsewhere (3). However no complete experimental data were reported for the mass and energy balance around the P.D.U. reactor. These results which are now presented below are required in order to assess the economic faisability of the process.

EXPERIMENTAL

A photograph of the Process Development Unit used in this study is shown in Figure 1 while a schematic is depicted in Figure 2. The reactor is a multiple hearth furnace, with six hearths, 2 m high by 0,7 m in diameter. Heat transfert is provided through heating elements which are immerged in ceramics.

At the onset of an experiment wood chips are poured batchwise in a hopper which sits on top of the reactor. The hopper is equipped with a feeding device and is hermetically sealed. For the experiments herein reported, 6 kg of wood chips with a granulometry 1/4" - 1/2" Tyler Sieves was fed at a constant rate of 0,8 kg h^{-1} in the reactor. Residence time of the solids in the reactor was approximately 30 min.

A mechanical vacuum pump draws the organic vapor and gas products from the reactor through a series of outlet manifolds installed along the reactor cylinder. The maximum absolute pressure in the system was lower than 30 mm Hg. The condensable vapors are received in a train of jars which serve as condensation units at the bottom of the primary cooling unit. The primary cooling unit used circulating tap water as cooling medium. The first receiver was let at room temperature. The second receiver was immerged in a circulating bath of water/ethylene glycol mixture. The third receiver was immerged in a bath of dry ice/acetone mixture while the last receiver was filled with glass wool at room temperature.

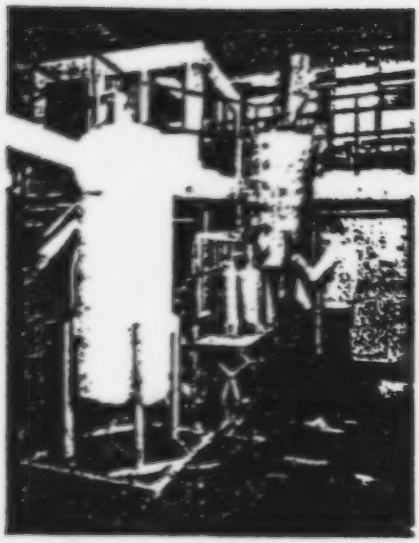

Figure 1: Photograph of the vacuum pyrolysis P.D.U.

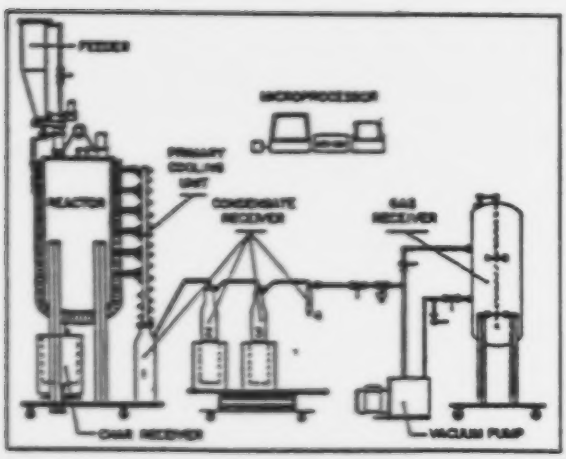

Figure 2: Schematic of the vacuum pyrolysis P.D.U.

The noncondensable gases (H_2, CO_2, CO, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and a few other minor components) are continuously pumped in a 500ℓ metallic vessel which was set under a vacuo at the beginning of a test run. The gas phase, which is continuously mixed by an agitating device within the receiver, is periodically sampled and analyzed with a gas chromatograph.

The solid residues are directed towards the bottom of the reactor, being moved by a series of rattles attached to the main rotating shaft of the reactor. The residual char is received in a metallic jar which is installed on a load cell. Temperature of the falling char is continuously recorded.

At time zero of a test run, wood chips are introduced in the preheated reactor. For the experiments herein reported, set-point temperatures of the hearths varied between 250° and 450°C, with increasing temperature from top to bottom of the reactor. The radial temperature gradient for any heating plate was lower than 3°C during a run.

The P.D.U. was attached to a central microprocessor which simultaneously permitted data acquisition and control of the operating parameters. Apart from temperatures, the system also enabled control of pressure in the system. Control of the feedstock flowrate from the hopper and control of the residence time of wood chips on each hearth of the reactor was automatically performed with the microprocessor. This unit also enabled continuous monitoring of power consumed by the equipment used. Air leakage through the system was determined to be lower than 0,7 torr h^{-1}. This value was computed in the mass balance calculations.

The experiments conducted on the P.D.U. were performed with Populus euramericana. The hybrid poplar I 45/51 clone was obtained in form of chips from Forintek Canada Corp., Ottawa. The stands were 8 years old, with an average height of 10,7 m and an average diameter at breast height of 11,4 cm. It's elemental composition was determined to be 48,6% C, 6,2% H, 0,1% N and 45,1% O. The proximate analysis gave 0,6% ash, 82,4% volatile matter and 17,0% fixed carbon. The gross calorific value of the wood used was 4700 kcal kg^{-1}, on a dry basis. Moisture of the air-dry feedstock was on the average 7,0%.

A batch unit has also been used to provide data for the vacuum pyrolysis of various hardwood and softwood species. The 10ℓ unit had a capacity of about 0,6 kg of air-dry wood chips, sieved to 1/8" - 1/2" Tyler mesh. The unit enabled withdrawal of the vapor and gas product by the top of the reactor. The final temperature reached for the experiments herein reported was 455 °C, at a maximum absolute pressure lower than 30 torr. Unless specified, the feedstock bed height in the chamber was 13 to 14 cm. Details regarding the description and operation of this laboratory scale batch unit will be found elsewhere (8).

RESULTS - DISCUSSION

P.D.U. Operation

A series of three runs with almost identical operating conditions as reported in the previous section were conducted on the P.D.U. One run was extended over a longer period of time, prior and after the run test itself, in order to determine the energy requirements for the pyrolysis reaction. Data for gas pressures, weight of char, hearth temperatures, power and total consumed energy have been recorded for this run as a function of time. The results are presented in Figures 3 to 7 of the paper.

Figure 3 below shows the variation of both the reaction pressure and the noncondensable gas pressure in the gas receiver as a function of time. The reaction pressure was read prior to the condensation unit, in the reactor itself. The run itself (wood is fed) occurred between time 33 and 44, as indicated on the Figure. The reactor pressure raised from 10^{-1} torr at the onset of the run up to approximately 20 torr, peaking for a while around 30 mm Hg. The gas pressure in the reservoir at the outlet of the vacuum pump steadily built-up, which reflects the smooth operation of the run.

Figure 4 illustrates variation of the weight accumulation of char in the char receiver as a function of time. The ups and downs on the curve prior to the run itself are due to pressure variations in the system which in turn influenced the stability of the load cell. This problem along with the offset at the beginning of the run will be solved in the future. The steady weight increase of char in the reservoir is again noticeable.

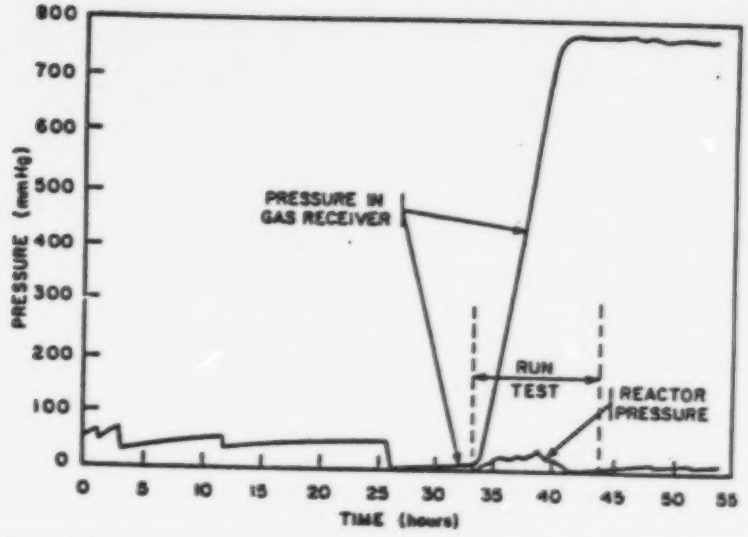

Figure 3: Variation of pressure in reactor and gas receiver as a function of time.

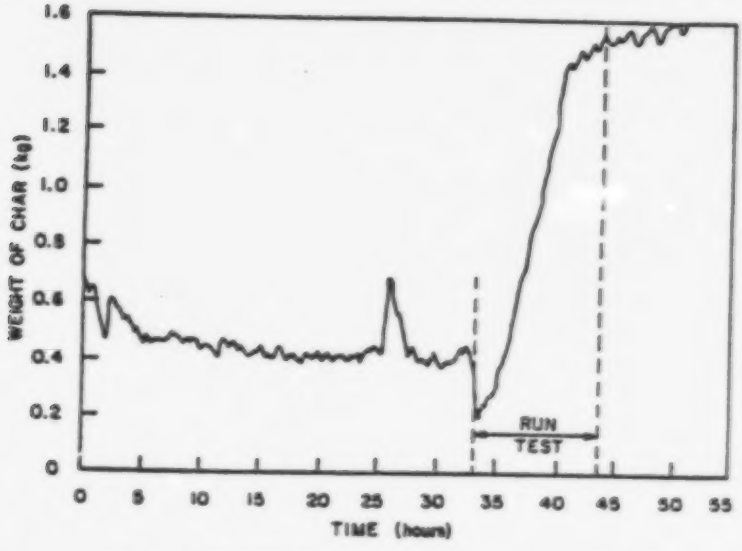

Figure 4: Weight accumulation of char as a function of time.

Variation of hearth temperatures as function of time is illustrated in Figure 5 and 6 below. Figure 5 is an overview of the hearth temperature patterns from time zero until the end of the experiment, 55 hours latter. The Figure illustrates the transitory heating up stage from time zero until the temperatures are well stabilized, some 25 hours latter. The run test itself was performed at time 33, ending at 44. The enlargement of the curves during the run, as indicated by the square on Figure 5, is presented in Figure 6 of the paper. Figure 6 at the bottom shows the sharp decline in temperatures for hearths 1 and 2 which are located near the top of the reactor. The decrease in temperature can be attributed to endothermal reactions occuring during this stage of pyrolysis. On the contrary, temperature for hearths 3, 4 and 5 (middle and upper Figure 6) increased after the introduction of biomass in the reactor, which can be attributed to exothermal reactions. Temperature for hearth 6 (upper Figure 6) slightly declined after the feeding of wood. The initial steady state temperature conditions were recaptured after the run, when no more wood or char was left in the reactor.

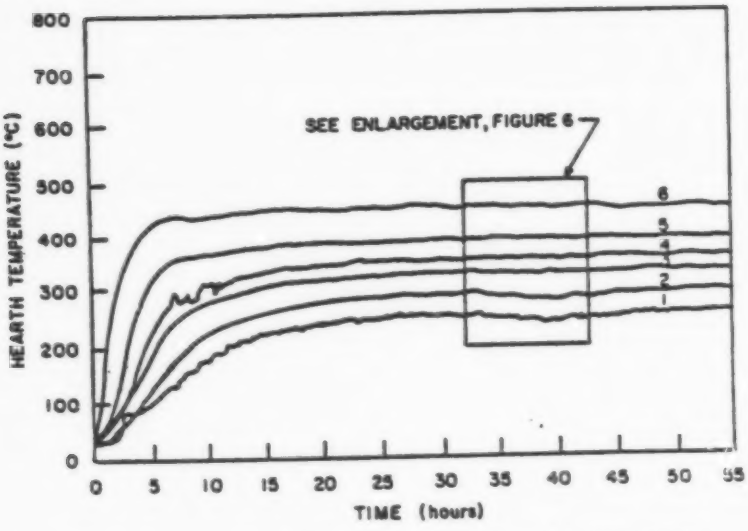

Figure 5: Variation of hearth temperatures as a function of time.

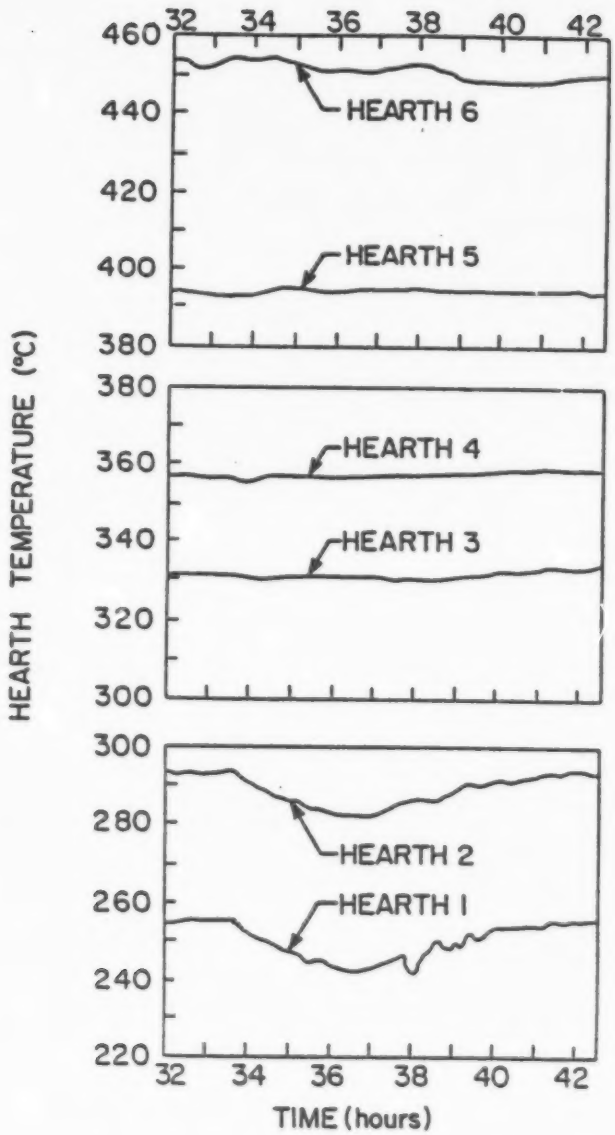

Figure 6: Variation of hearth temperatures as a function of time (Enlargement for part of Figure 5).

Mass balance

The hybrid poplar clone I 45/51 was selected for comparaison purposes. The mean product yields along with their standard deviations in parentheses were determined to be the followings, on a % weight, organic wood basis:

Oils : 46,7 (1,0)

Char : 23,6 (2,8)

Water: 17,6 (0,8)

Gas : 12,1 (0,4)

The mass balances closed within 4% for this set of experiments in the P.D.U. Losses were distributed at pro rata of products.

The gas phase was mainly composed of carbon dioxide and carbon monoxide. The low temperatures reached prevented the formation of substantial amounts of hydrogen, methane and light hydrocarbon gases. The average composition of the major gas components is given below, on a % wt., organic wood basis:

CO_2 : 7,3 (0,3)

CO : 3,9 (0,4)

CH_4 : 0,3 (0,1)

Others: 0,6 (0,1)

The minor gas compounds mainly included ethene, ethane, proprene and butene. The calorific value of the gas phase was low, 1750 kcal kg^{-1} (2270 kcal Nm^{-3}).

The wood-derived liquids were recovered in a series of condensers as depicted in Figure 2. The condensing temperatures were selected so that water (moisture and pyrolytic water) was mainly recovered in receivers 2 and 3 of the system. The relative amounts of liquids recovered in each of the receivers are reported below along with their water contents:

	Receiver No			
	1	2	3	4
% wt. of total liquids	37	48	13	2
Water content in each receiver (% wt.)	5	60	50	1

It was found later that complete elimination of water in the first receiver was possible through a closer control of both the cooling temperature of the primary cooling unit and the system pressure.

Effect of bed height

The high yields of pyrolytic oils obtained with the P.D.U. set-up are in range with the results found on vacuum pyrolysis of various hardwood and softwood species in a laboratory scale batch unit (see Table 1). However the oil yields derived from P. euramericana in the P.D.U. were significantly higher that those obtained with the batch unit as indicated in Table 1.

In the P.D.U. reactor, height of the moving bed of wood chips varied between 1 and 3 cm. In the batch unit height of the fixed bed was 13 cm (bed diameter: 20 cm). The lower value of oil yield in the batch unit was partly attributed to repolymerisation/recombination reactions of wood tar on the forming-char particles. This was confirmed by a subsequent run conducted in the batch unit with a bed height of P. euramericana of 1 cm (see Table 1).

When comparing the overall results of the 1 cm experiment in the batch unit with those from the P.D.U., it is observed that the yields of char and pyrolytic water are similar, while apparently the relatively smaller metallic chamber of the batch unit induced cracking of the vapor macromolecules into noncondensable gases. Overall, the influence of the bed height itself is small on the oil yield.

Oil characteristics

It was reported before that some of the chemicals (e.g., carboxylic acids and phenols) found in the organic liquid phase obtained on vacuum pyrolysis of aspen poplar have a potential market value if they can be easily separated from the bulk of the condensates (7). Experimental data which will eventually confirm or infirm this possibility will be available soon and should be reported elsewhere (9). Qualitative (5) as well as quantitative (2, 4, 7) analyses of these oils will be found in other publications.

Table 1: Vacuum pyrolysis of various wood species in a batch unit.*

	POPULUS EURAMERICANA (1) cm bed)	POPULUS EURAMERICANA (1 cm bed)	THUJA OCCIDENTALIS	PICEA RUBENS	PICEA GLAUCA	ABIES BALSAMEA	LARIX LARICINIA
YIELDS (% wt., wood m.a.f.b.)							
Oils	39,8	42,4	50,1	45,6	46,9	40,3	39,6
Char	24,8	21,8	22,8	23,8	23,4	26,7	29,0
Water	19,8	19,5	16,4	18,6	18,0	18,2	20,9
Gas	15,6	16,3	10,7	12,0	11,7	14,8	13,5
GAS COMPOSITION (% wt., wood m.a.f.b.)							
CO_2	8,9	9,2	5,9	6,5	6,4	7,6	6,4
CO	5,3	4,5	3,9	4,1	3,8	5,3	4,6
CH_4	0,7	0,5	0,5	0,8	0,7	0,8	1,2
C_nH_m	0,3	0,2	0,2	0,3	0,3	0,4	0,4
Others	0,4	1,9	0,2	0,3	0,5	0,7	0,7

*Final temperature: 455°C. Absolute pressure: < 50 torr

Table 2 below illustrates some properties of the solid and liquid products obtained on vacuum pyrolysis of P. euramericana in the P.D.U. Both the char and oil (from the first receiver) materials represent upgraded fuel products as compared to the initial raw material. It can be noted that the calorific value of the condensates is strongly dependent on the water content.

Table 2: Properties of solid and liquid products obtained on vacuum pyrolysis of Populus euramericana in the P.D.U.

	WATER	PROXIMATE ANALYSIS (% wt)			ELEMENTAL ANALYSIS (% wt)				GROSS CALORIFIC VALUE
	(% wt)	Ash	V.M.	Fixed C	C	H	N	O	(kcal kg^{-1})
WOOD FEEDSTOCK	7,0	0,6	82,4	17,0	48,6	6,2	0,1	45,1	4180
CHAR	2,8	2,8	27,9	69,3	78,1	3,6	0,3	18,0	6990
OILS (1st receiver)	3,8	-	-	-	54,0	6,8	0,2	39,0	5270
AQUEOUS PHASE (2nd receiver)	55,0	-	-	-	37,9	8,6	0,5	53,0	*

*Could not be ignited. An analysis performed by Battelle-Northwest Lab. in Richland, Washington, on a similar vacuum oil product containing 38,5% water gave 3300 kcal kg^{-1} (2).

It has been reported (10) that the corrosive properties of pyrolytic oils derived from biomass would preclude some of its industrial uses. The new data reported in Table 3 below tend to lessen the full significance of this statement. The condensates produced during the P.D.U. runs were subjected to standard corrosion tests (ASTM-G-1/1981 and G-31/1979). In the Method, a metallic plate made of the material to be tested is immerged during several hours in the corrosive liquid. The test was conducted in beakers at room temperature, without any agitation of the liquid mixtures. No nitrogen was bubbled through the samples. Weight loss of the metal was periodically determined.

The results are expressed in m.p.y. (mils/year). The following classification was derived from corrosion data tables (6). It was used as a guideline in order to evaluate the corrosive properties of pyrolytic oils.

	m.p.y. <	2	not corrosive
	m.p.y. <	20	slightly corrosiv
20 <	m.p.y. <	50	corrosive
	m.p.y. >	50	highly corrosive

Tests were performed with the oil phase (from receiver No 1) which contained small amounts of water and the aqueous phase (from receiver No 2) which contained substantial amounts of water. Results are presented in Table 3. The Table shows that the carboxylic acid content of the tested materials was not significantly different from one sample to the other.

Table 3: Corrosion properties of wood-derived oils.

	Water (% w/w)	CARBOXYLIC ACIDS (% w/w)			AVERAGE m.p.y.		pH
		Formic	Acetic	Propionic	Steel AISI C 1015	Stainless Steel AISI 304	
Dry oils (Receiver No 1)	1	2,3	2,8	8,7	5,4	<2	*
Oils (Receiver No 1)	5	3,7	3,8	-	42	<2	1,5-2
Aqueous Phase (Receiver No 2)	80	3,1	3,7	8,8	258	<2	1,1-1,5
Acetic acid (18 %w/w)	88	-	18	-	387	<2	3,1

* Undetermined

According to the classification Table, the aqueous phase from receiver No 2 was found to be highly corrosive when standard steel was used while the organic phases were much less corrosive. However the corrosivity dropped dramatically with decreasing amounts of water. Neither mixtures exhibited significant corrosion activity in presence of stainless steel.

These results strongly suggest that water played a major role in the corrosion activity of pyrolytic oils. Further studies along this line are underway in order to substantiate these data.

Reaction heat requirements

Based on the mass balance and product analysis reported before a calculation was made in order to determine the calorific value distribution following wood thermal conversion. On a moisture-free basis, 95% of the calorific value originally contained in wood was recovered in the solid, liquid and gaseous products. The water-free oils amounted to 58% of the total calorific value of the products, that of char amounted to 37% while the gas phase only reached 5% of the total.

One objective of this study was to estimate the heat required to conduct the vacuum pyrolysis reactions. The equipement used enabled such measurement. The principle used was to maintain the hearth temperature set-points at pre-determined values while measuring the amount of electrical energy consumed as a function of time.

Figure 7 shows the variation of power consumed by the P.D.U. (exclusive of the heat required by the cooling units) as a function of time. At the beginning the energy consumed was mainly used for heating up the reactor. After a while, the energy consumed was used to compensate for the heat losses outside the reactor. At this point, hearth temperatures remained constant (see Figure 5). Five different stages can be observed in Figure 7. Stage A lasted 10 hours and represented the heating up phase. Stage B, the stabilisation period, followed for the next 7,5 hours. Next a blank test was run at stage C during 13,5 hours. During that stage, all operating parameters were identical to those of the following stage, except that no wood had been introduced in the reactor. The average power consumed by the system during stage C was determined to be relatively stable at 3748 W. The electrical power consumed during that stage was essentially used to compensate for the heat losses outside the reactor. The initial steady state conditions were recaptured after the run, at stage E, when no more wood or char was left in the reactor. The average power value for stage E was compared with that of stage C, prior to the run test. The former value was determined to be almost identical, at

3750 W, which was another indication that the system had reached a steady state regime identical to that prior to the feeding of wood.

The voltage variation which occured over a period of 55 hours in the pilot room was taken into account when conducting the power measurements. Voltage varied between 230,9 and 241,4 V, averaging 237,1 V. Measurements were automatically made each 60 sec.

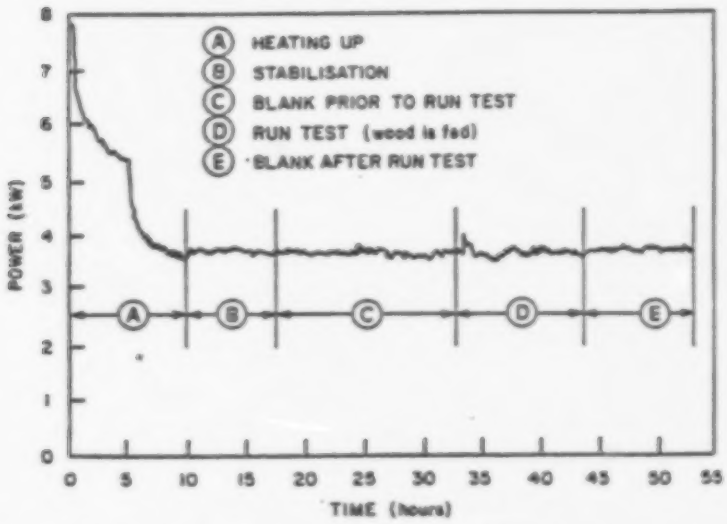

Figure 7: Variation of power consumed by the P.D.U. as a function of time.

Stage D features the run test itself where the wood feedstock gave an impulse to the system. The total energy consumed during that period which lasted 11 hours was determined by integrating the corresponding area under the curve on Figure 7. The resulting value was found to be lower than the corresponding value for stages C and E which solely accounted for the heat loss. The statistical significance of this result was estimated by comparing the electric power consumed at any time during the run with both the highest and the lowest power values recorded during either blank stages C or E. The range of variation of total energy used

for conducting the reactions was comprised between the borderlines given by

$$\int_{33}^{44}\left(P_{RUN} - P_{BLANK\ MIN.}\right)dt \quad \text{and} \quad \int_{33}^{44}\left(P_{RUN} - P_{BLANK\ MAX.}\right)dt$$

The result is shown on Figure 8 where it is observed that the total energy required is comprised within a small interval around the zero energy level. At the end of the run (since this is an integration process, the error is cumulative) the variability was found to be ± 552 W.h around the mean value (-307 W.h).

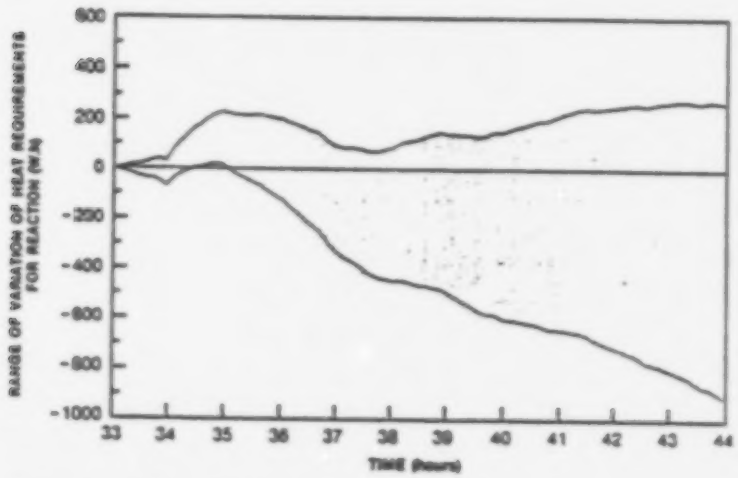

Figure 8: Range of variation of heat requirements for reaction as a function of time.

This total excess mean energy was generated on vacuum pyrolysis of 6 kg of wood chips at 7% moisture. On a moisture - free basis, the mean value was calculated to be 95 kcal kg^{-1}. As a whole, this represents only about 2% of raw wood calorific value. A better measurement of the wall temperatures of the reactor should permit in the future to reduce the variability of the data and improve precision of the result.

OIL UPGRADING STUDY

A collaborative research program between researchers at the Université Laval and those in Sherbrooke is currently

underway whereby two processes are considered for the upgrading of pyrolytic oils.

The first deoxygenation process involves the hydrotreatment of oils in a one liter autoclave in presence of Co-Mo/γAl_2O_3 catalyst under high pressure of H_2 + CO. Deoxygenation is difficult due to the high O content of pyrolytic oils which tend to polymerize in presence of high organic acid contents. Experiments conducted at 200°C under autogenous pressure have shown that polymerization can be partially controlled by mixing the oil with 5 to 20% by weight of methanol. Under hydrotreatment conditions at 300°-350°C however, polymerization still occurred. The current study is aimed at achieving shorter residence times of the oil mixtures in the reactor under fast hydroconversion conditions.

Another deoxygenation approach under consideration involves contacting the vapor phase organic macromolecules with H- or modified forms of the ZSM-5 zeolite. A recent study has shown that severe coking occurred when oil is fed as a liquid in the reactor (1). The contemplated approach would make use of the vapor phase fractionation allowed by the vacuum pyrolysis equipment to isolate the lighter fraction of the pyrolytic oils which would not lead to coking. It is known that small aliphatic acid molecules, esters, ketones, aldehydes... all yield in presence of ZSM5 C_2-C_{10} hydrocarbons with a large portion of the O being retrieved as CO_2 as well as H_2O. Another advantage of this upgrading process is that significant amounts of water in the feed can be tolerated without large detrimental effects on the acid catalysis activity.

CONCLUSION

The experimental results obtained in a large, semi-continuous vacuum pyrolysis equipment are in line with the preliminary data obtained in small batch units. Pyrolytic oil yields in the range of 50% w/w have been confirmed. The energy requirement for conducting the pyrolytic reactions is close to zero for this process. Future work should involve the determination of the rate of heat transfert.

ACKNOWLEDGMENTS

This study has been supported by Energy, Mines and Resources Canada and the Natural Science and Engineering Research Council Canada.

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DISCUSSION

W. Walawender, Kansas State U.: You mentioned that you had four separate receivers for liquid collection. What temperature differences were involved between those four?

Roy: For the first receiver, we used hot water at 50°C; for the second receiver, we used ethyleneglycol; the third receiver was dry ice-acetone at -78°C; and the fourth receiver was at room temperature.

Walawender: In the first experiments, everything was collected together?

Roy: With some separation according to condensation temperature.

Walawender: What was the appearance of the condensate in the first receiver?

Roy: Very fluid at room temperature, and of course a small amount of water. On a dry water-free basis, it was still fluid. It contains a lot of oxygen as expected.

Walawender: But you didn't observe any settling?

Roy: Very little.

Walawender: No material was formed that was essentially semi-solid at room temperature?

Roy: It was liquid at room temperature.

D. Scott, U. of Waterloo: Your corrosion results are very interesting, but there's one additional ingredient that is necessary for the corrosion rates you listed. That is oxygen. If you don't have oxygen present, we found the liquids are essentially non-corrosive to steel.

Roy: You've done tests by bubbling oxygen through the liquid?

Scott: No, I'm just speaking from our experience.

Roy: We want to make sure of the data by doing tests at 40° or 70°C. Your comment about oxygen is a good one too.

Scott — We've examined a variety of materials in our unit and there's been no corrosion, even on mild steel.

D. Punwani, IGT — How is your process different in terms of product yield and quality compared to the French process? In the condensate, you have four condensers at different temperatures so the water and the hydrocarbon content in those condensers are different. What about the total oil yield and the quality of the char you get?

Roy — The liquid yield is about twice that of the French process, the purpose of which is to produce charcoal. The liquid is a byproduct, which consists of an acid fraction containing mainly carboxylic acids. In our case, char is the byproduct. Our unit operates mainly to produce liquids, which are obtained at different outlets along the reactor. We hope to get phenolic compounds derived from lignin at the bottom, and the water and acidic compounds at the top of the reactor. The French, on the other hand, use a separate distillation unit to separate the acids.

Punwani — I know you do not have any analysis of the aqueous phase, but have you measured its COD or BOD?

Roy — We have previously reported the chemical analyses of these liquids, but we have not evaluated it in terms of environmental criteria. We have reported percentages of perhaps 50 compounds in these pyrolytic oils.

C. Mickel, Technical Insights, Inc. — What agricultural residues have you tested? Have you characterized the chemicals produced as compared to those from wood?

Roy — We have tested Agriculture Canada corn stover, wheat straw, and oat straw. The yields are a little bit lower in these cases, in the range of 30% to 40%, rather than 40% to 50%. But we have not analyzed these chemicals as extensively as those from wood. Although the heating values are similar, the problem with agricultural wastes is carbonization. Since they are not dense materials, the unit is almost empty. So perhaps a fluidized bed approach would be better

than a reactor like ours for the pyrolysis of agricultural residues. Don, maybe you can comment on that.

Scott

It's very difficult to feed noncompact residues into any kind of reactor. But I hear Agriculture Canada has just decreed that straws from grain lands are no longer agricultural wastes; they have to be plowed back in.

Pohland

Can you tell us what it would take to make this process usable in industry?

Roy

What is needed is to look at the heat transfer problems to improve the throughput in the system, and to prove or disprove that we can isolate fractions of liquids out of the reactor. We believe we can answer these questions 2 to 3 months from now. As an alternative to recovering condensates, we are working on upgrading these oils by hydrotreatment with zeolites in the vapor phase right at the outlet of the reactor to produce hydrocarbons. We are doing that work with Serge Kaliaguine at Universite Laval, so this could represent a real breakthough. The problem is the rate at which the liquids repolyermize, which is faster than the deoxygenation process, so we have to have better kinetics. Upgrading will be better if done in the vapor phase.

Symposium Papers

Energy From Biomass and Wastes IX

Presented
January 28 — February 1, 1985
Lake Buena Vista, Florida

Symposium Chairman
Donald L. Klass

Sponsored by
Institute of Gas Technology
IIT Center, 3424 South State Street
Chicago, Illinois 60616

Price: $100.00
ISBN 0-910091-53-6
• Copyright by the
Institute of Gas Technology
December, 1985
Printed in U.S.A.